Electrochemical Industry

VOL. I. PHILADELPHIA, JANUARY 1, 1903. NO. 5.

Electrochemical Industry

Published on the first of each month by the

ELECTROCHEMICAL PUBLISHING COMPANY,

[*Incorporated.*]

CITY TRUST BUILDING, PHILADELPHIA, PA.

J. W. RICHARDS, PH.D.....*President.*

E. F. ROEBER, PH.D.....*Editor.*

Long Distance Telephone 3-51-24.

Subscription Price: $2 per year, postpaid to any part of the world. Single copies, 25 cents.

ADVERTISING RATES GIVEN ON APPLICATION.

Copyrighted, 1903, by the Electrochemical Publishing Co.

Application made for Entry as Second-Class Matter at the Philadelphia Post-Office.

CONTENTS

Editorial 153
Castner Memorial Tablet 156
Electrolytic Processes 156
Electrolytic Refining of Gold. By D. K. Tuttle..... 157
The Present Metallurgy of Aluminium. By J. W. Richards..... 158
A French Plant for Making Steel in the Electric Furnace..... 162
Some Laboratory Observations on Aluminium. By C. F. Burgess and Carl Hambuechen..... 165
Table of Electrochemical Equivalents and Their Derivatives. By Carl Hering 169
Aluminium as a Reducing Agent in Metallurgy. By G. P. Scholl.. 175
Why the E. M. F. of the Daniell Cell Changes with the Density of the Solutions. By H. S. Carhart..... 178
Two German Plants for Sterilizing Water by Ozone..... 179
Synopsis of Articles in Other Journals. By Carl Hering..... 181
Analysis of Current Electrochemical Patents. By G. P. Scholl..... 186
Current Notes 192
Correspondence: Faraday's Law and the Theory of Electrons. By H. C. Cooper..... 192
Book Reviews 193
A New Acetylene Lamp..... 194
1,500 Ampère Switch 195
Porous Diaphragms 195
Digest of U. S. Patents Prior to July, 1902 (Alkali Processes). By Byrnes & Townsend..... 196

ALUMINIUM.

In this issue we publish three articles on the manufacture, the properties and the uses of aluminium. In 1854, Prof. Deville, of Paris, succeeded in obtaining metallic aluminium by electrolyzing the fused double-chloride of aluminium and sodium. In those days, however, electrical energy was expensive, as primary batteries were then the only means of generating an electric current; and Prof. Deville concluded that the electrolytic method could not compete with purely chemical methods. It is amusing to note how completely the situation is now changed, since electrical energy became cheaper and the processes of Hall and Heroult were introduced into practice on a large scale. The article by Dr. J. W. Richards, who has been intimately connected with the development of the aluminium industry, will engage the attention of our readers, as it gives interesting historical notes on the work of Hall and Heroult, together with a discussion of the scientific principles of their process.

Prof. C. F. Burgess and Mr. Carl Hambuechen give an account of valuable laboratory observations on aluminium. To utilize aluminium to greatest advantage, one must be familiar with its particular properties, and especially with its almost ever-present surface coating. The authors show how this coating introduces peculiar difficulties in various processes, like soldering aluminium, plating on aluminium, etc., and they also show the means of overcoming these difficulties. Electroplating upon aluminium should have a great commercial field for certain utensils. On the other hand, the problem of plating with aluminium seems to resolve itself into the problem of finding a suitable solvent which will dissolve an aluminium salt and at the same time will not chemically react with the deposited metallic aluminium. It seems certain that water as a solvent does not do.

The third article in this issue on aluminium is by Mr. G. P. Scholl, on the use of aluminium as a reducing agent in metallurgical processes. That aluminium is a very strong reducing agent has long been known, but there was no use of working out the details of such a process, as long as aluminium itself was expensive. The decrease of the price of aluminium paved the way for Dr. Goldschmidt's important process. In this connection we may note that calcium carbide has similarly been tried as a reducing agent in recent years. These are only special cases of the general rule that electrochemical processes enable us to store up energy in producing chemicals which may afterwards be used as reagents in other processes.

ON FARADAY'S LAW.

In this issue we print two contributions relating to Faraday's law; a long article by Mr. Carl Hering, and a brief communication by Dr. H. C. Cooper. Dr. Cooper refers to an

article published in our November issue on Faraday's law and the theory of electrons. In this article it was shown that Prof. O. C. Johnson's well-known notation of positive and negative bonds may easily be applied to electrochemical calculations, because his positive and negative bonds may be considered to correspond to positive and negative charges. In electrochemical processes the change of valency in Johnson's sense is nothing else but the giving off or receiving of electric charges at the electrodes. Prof. Johnson's old notation may therefore be interpreted as an expression in different words of what is now generally assumed to be the mechanism of the transport of electricity through an electrolyte by means of charged ions.

Dr. Cooper appears to consider it preferable for didactic reasons to put the latter mental picture at the head of such considerations. He appears to object to the use of the word bond. But whatever may be thought about bonds and valency in the light of recent investigations, we do not see any possible way to evade the idea of valency in electrochemical action and in the application of Faraday's law. It does not seem possible to describe the chemical action at the electrodes of an electrochemical cell otherwise than as reduction and oxidation (or as Dr. J. W. Richards says, "perduction"), that is, as changes of valencies. Of course, one might use other terms, but we do not see what useful purpose could thereby be accomplished. Even Dr. Cooper, after having expressed himself against the use of the terms bond and valency, uses, in the expression of Faraday's law, the term "equivalent amounts." With the essential contents of Dr. Cooper's explanations we fully agree; in fact, he states the views expressed in our former article on Faraday's law and the theory of electrons, only in different words, by carefully evading the term chemical bond and substituting for it at once the idea of an electric charge. This is in absolute agreement with the sentiment expressed in our former article.

Mr. Carl Hering's article will certainly be extremely welcome to the rapidly increasing number of workers in the electrochemical field. Faraday's law is the foundation of every calculation in electrolytic processes, and a table which simplifies these calculations and saves time is, of course, of great value to the busy practical man. The table is also to be heartily recommended as being the result of a complete and careful recalculation of the electrochemical equivalents, based upon the most recent and best fundamental values; moreover it contains columns relating to the energy, which we believe are not to be found in any other table and which may often be used to advantage in practice.

In the text which accompanies his table, Mr. Hering illustrates the use of his table by a series of typical examples, well chosen, in order to show the great variety of possible cases. This text is, in fact, a concise treatise on Faraday's law, and the student who reads it carefully and recalculates the various examples should be highly benefited. We desire to add a few remarks on the relation between the methods of calculation, described by Mr. Hering and that in which the ionic charge is used as a basis; and some further remarks on the interconnection between the two methods, described by Mr. Hering.

The method of calculation, which is based on the ionic charge, is perhaps the safest for anyone familiar with the idea of charged ions in all but the simplest cases. The method is to first find the equation which represents the complete electrochemical action; this action is necessarily a reduction at the cathode and a "perduction" (or oxidation) at the anode. In the sense of the ionic theory the reduction at the cathode is a loss of positive charges given off to the cathode; monovalent ions (like H) give off one charge; bivalent (like Cu in $CuSO_4$) two charges, etc. The perduction at the anode is a gain of positive charges (or a loss of negative charges); the zinc atom which goes into solution in the Daniell cell is changed from an atom to an ion and thus gains two charges. It is evident that the number of charges received from the anode in any given time must be exactly equal to the number of charges given off to the cathode in that time. When the equation representing the whole reaction has thus been found, and when it has been determined how many charges are received from the anode and given off to the cathode, then one has simply to remember that each such charge represents 96,540 coulombs, if the chemical symbols in the equation represent gram molecules or gram atoms or gram ions. The further calculation is then very simple. There is no essential difference between this method and the method based upon the change of valency in connection with the table, but there is this practical difference: the former method requires some calculations which are avoided by the use of the table.

One point might, however, be emphasized. While the valency is generally considered in text-books to be the determining factor in calculations with reference to Faraday's law, Mr. Hering speaks of the *change of valency*, instead of the valency itself. This is strictly correct, and the ionic theory takes exactly the same view. For instance, if at an inert cathode ferric sulphate is reduced to ferrous sulphate, the change of valency of Fe is from three to two, the difference being one. From the point of view of the ionic theory, a three-valent Fe gram ion has a charge of three times 96,540 coulombs and a bi-valent Fe gram ion has a charge of two times 96,540 coulombs; hence the change from a three-valent to a bi-valent gram ion Fe corresponds to giving off 96,540 coulombs to the cathode.

Finally we will point out the interconnection between the two methods, discussed in Mr. Hering's article. The one consists in taking the change of valency and reading the amount perduced at the anode or reduced at the cathode directly from the table. The other method, which he calls the older chemical method, requires the exact knowledge of the equation representing the total electrochemical action. It is, of course, self-evident that both methods must be essentially one and the same, but there is one point which, at first sight, may appear a puzzle to the student. In "the older chemical method" one must know the co-efficients of the different terms entering into the equation of the electrochemical reaction. In the other method nothing is required but a knowledge of the change of the valency, and Mr. Hering even gives an example to show that the co-efficients in the equation of the reaction may be ignored. It is self-evident that this puzzle can be solved only by proving that there is a distinct relation between

the co-efficients of the equation and the numbers representing the change of valency at both electrodes.

Now this relation is nothing but the old well-known rule given by Prof. O. C. Johnson for balancing an equation which represents a process involving oxidation and reduction. This means that if we know the change of valency of the element reduced at the cathode (for instance, say, three) and the change of valency of the element perduced at the anode (say two), then we know the co-efficients with which these elements enter into the equation representing the total electrochemical reaction. In our special case this co-efficient is two for the former (reduced) element and three for the latter (perduced) element. As was pointed out in the article in our November issue, already referred to above, this rule becomes quite self-evident in the light of the ionic theory. In our special case it means that if the element reduced at the cathode gives off three positive charges to the cathode and the element perduced at the anode receives two positive charges from the anode, then it is necessary that two atoms are reduced at the cathode in the same time as three atoms are perduced at the anode, because only under this condition the same number of positive charges (six in this special case) pass from the anode into the electrolyte as pass from the electrolyte to the cathode.

PHYSICAL CHEMISTRY AND ELECTROCHEMISTRY.

In a recently published report of the Census Committee of the American Chemical Society, Dr. Louis Kahlenberg discusses the development of modern physical chemistry. He points out that it would be wrong to believe that physical chemistry has sprung up suddenly and has developed from the subjects of chemistry and physics in an unnatural or artificial manner; on the contrary, the very opposite is shown to be the fact, as the beginnings of physical chemistry date back to the very beginnings of chemistry. The founders of modern chemistry, the men that were so prominent during the latter part of the eighteenth and the former part of the nineteenth century, to a very large extent employed physical means to investigate chemical problems. And during the period of the development of analytical and organic chemistry, while attention was primarily directed to the end products of chemical reactions, yet nearly all of the physical means known to-day were used more or less extensively; the balance, the pycnometer, the thermometer, the retort, etc., and even the calorimeter, the spectroscope, the polariscope, the galvanometer, the refractometer and photometer were at times called into requisition.

Dr. Kahlenberg shows how the two sciences of physics and chemistry, at first practically one, became gradually more and more distinct, as the chemists were chiefly occupied in studying the end products of chemical reactions, while the physicists developed refined methods of exact measurement. And yet during this entire period there always were some men whose researches lay on the border line between the two sciences. The work of these men kept alive the intimate connection between chemistry and physics and forms the foundation of modern physical chemistry. Modern physical chemistry is distinguished from the older "pure" chemistry, not by the methods used, but by the object of investigation; the field is a broader one. Not only the end products of chemical action are studied, but also the processes of the formation of these products, together with all the concomitant energy changes that take place. Physical chemistry is thus general chemistry —chemistry of the most general kind. Dr. Kahlenberg concludes his remarks by appealing to physical chemists to bear constantly in mind the general aim of their work, which, like that of all sciences, is to minister to the welfare of mankind in the broadest and highest sense of the word. Science must have all avenues for its progress open; but it must be borne in mind that science is for man and not man for science.

We call attention to these remarks of Dr. Kahlenberg on the development and the aim of physical chemistry, because we want to make some similar remarks on electrocnemistry. Electrochemistry is often spoken of as the youngest branch of electrical engineering. This is correct as far as the industrial success is concerned. On the other hand, it should not be forgotten that electrochemistry is as old as electrical engineering. When Volta deviced in 1800 a cell by which chemical energy was changed into electrical energy, he was an electrochemist; and in 1807 Davy isolated the elements potassium and sodium by electrolysis of fused caustic soda and caustic potash and thus succeeded in bringing about new chemical reactions by means of the electric current. True, there was afterwards a long period in which industrial electrochemistry made practically no headway; but during this period, beginning with Faraday, the foundations were laid of modern theoretical electrochemistry.

It is out of place to sketch here the splendid development in recent years of industrial electrochemistry. The progress has been rapid and the success sweeping and the outlook for the future is very bright, especially as it becomes more evident every day that electrochemistry is only in the beginning of its industrial development, especially in this country with its enormous resources. The progress in future promises to continue to be rapid, but in order to be healthy, progress must be made on conservative lines. Industrial electrochemistry must remain in touch with theoretical electrochemistry and physical chemistry in general. It is a very good symptom—which was manifest to every one who attended the first two meetings of the American Electrochemical Society—that there is in this country good will and good feeling between electrochemical engineers and scientists, that both classes of electrochemical workers feel that they must stay together.

Electrochemistry is only a special branch of physical chemistry. Electrochemical scientists must be allowed to push forward on any road that seems to promise success. The roots of electrochemical science are in general physics and chemistry, and no progress in these sciences is so remote from the subject of electrochemistry that it should not be carefully watched by electrochemists. There is no pure science which cannot be eventually applied to the welfare of mankind. The practical man should not despise theories which at first seem to be "of scientific interest" only; and the theorist should never forget that as Dr. Kahlenberg puts it, science is for man, not man for science.

THE CASTNER MEMORIAL TABLET.

A distinguished audience attended the ceremonies of the unveiling of the beautiful bronze tablet in Havermeyer Hall, School of Mines, Columbia University, at 4 o'clock, on Tuesday afternoon, December 16, 1902. Addresses were delivered in the large chemical lecture room by Dr. Chas. F. Chandler, dean of the School of Mines and the professor under whom Mr. Castner studied chemistry for three years; by Dr. Marcus Benjamin, of the United States National Museum at Washington, who, as a classmate of Mr. Castner, related some personal reminiscences illustrating his characteristics as a student and investigator, and by Prof. Joseph W. Richards, of Lehigh

BORN BROOKLYN N·Y·
SEPTEMBER XI MDCCCLVIII
DIED SARANAC LAKE N·Y·
OCTOBER XI MDCCCXCIX
IN · MEMORY · OF
HAMILTON · Y · CASTNER
STUDIED · AT · THE · SCHOOL · OF · MINES
COLUMBIA · UNIVERSITY
FROM SEPTEMBER MDCCCLXXV TO JUNE MDCCCLXXVIII
HIS · CHEMICAL · INVENTIONS
MDCCCLXXXVI · CHEMICAL · PROCESS · FOR · SODIUM
MDCCCXC · ELECTROLYTIC · PROCESS · FOR · SODIUM
MDCCCXCI · MANUFACTURE · OF · ALKALINE · PEROXIDES
MDCCCXCII · ELECTROLYTIC · PROCESS · FOR · SODA
AND · CHLORINE
MDCCCXCII · BLEACHING · COMPOUND
MDCCCXCIII · ELECTROLYTIC · APPARATUS
MDCCCXCIV · ELECTROLYTIC · PROCESS · AND
APPARATUS · FOR · SODA · AND · CHLORINE
MDCCCXCIV · PROCESS · FOR · CYANIDES
MDCCCXCVI · GRAPHITISED · ANODES · FOR · ELECTROLYSIS

University, representing the American Electrochemical Society. Dr. Chandler related the history of the inception and development of Mr. Castner's inventions, while Dr. Richards discussed more particularly the relation of Castner's work to the aluminium industry, the general question of his pioneer work in electrochemistry and the effect of his inventions on industrial and economic progress. The audience then filed into the corridor, where, in the presence of Mrs. Castner and the company which had gathered to do her husband honor, Dr. Chandler, after a few impressive and appropriate words of dedication, drew aside the curtain.

ELECTROLYTIC PROCESSES.

In his presidential address delivered before the (British) Institution of Electrical Engineers, Mr. James Swinburne makes some very interesting remarks on electrolytic processes.

"This [electrolysis] is a branch of industry in which it is very difficult to tell our limits. In electrolytic copper-refining our limit is that of the copper wanted. Our electrolytic industries suffer mostly from the limits of intelligence of the investing public. It is assumed that we cannot do electrolysis in England because we have no water-power. This is only an excuse for inactivity. As already* explained, we can do just as well without water-power. A blast furnace is much more valuable than a waterfall of similar power, because it is near coal and in an industrial district. Moreover, as already explained, the cost of electrical energy is a small portion of that of most electrolytic products. At first electrolysis was to be applied to copper refining, then to caustic soda.

"The output of electrolytic caustic is really rather limited by the demand for bleach. What is urgently wanted is some other way of storing and carrying chlorine. Steel bottles and compression plant are an unsatisfactory solution. What are the limits in the way of electrolyzing fused salt? They are all incidental limits. The containing vessel is a difficulty. Sodium vapor attacks all silicates. Sodium distills near the temperature of fused salt. If not volatilized it forms a conducting bridge from the cathode. It attacks iron, though slowly. Hot porcelain and earthenware conduct electrolytically—as, by the way, the maker of electric frying pans knows—hot chlorine attacks metals, even when dry, and hot carbon cannot be exposed to the air. In addition, sodium, and perhaps chlorine, are soluble on hot salt, and traces of sulphate in the salt act as carriers, as sulphate and sulphide. I could a tale unfold if I read out laboratory notes of sodium experiments on a large scale. The difficulties are all incidental though, and I have little doubt electrolytic sodium at a low price will be in the market soon, and will affect profoundly many chemical and metallurgical industries. I would like an opportunity to continue experiments myself, but others will, I feel certain, soon succeed.

"In metallurgy electrolytic solution processes are in use or on trial for the more valuable metals, such as copper and nickel. The reaction between chlorine and metallic sulphides at high temperatures brings the whole domain of sulphide ores under our sway. Thus a sulphide, say galena, is treated with chlorine, which gives off the sulphur, as sulphur which is condensed and sold, making chloride of lead. The silver is extracted by stirring with a little lead, and the fused salt is then electrolyzed, yielding pure desilverized lead and chlorine. The process is thus self-contained, yielding sulphur, lead and silver. It is specially applicable to mixed refactory ores which are now nearly valueless and very plentiful, and contain much metal content, such as the mixed lead-zinc sulphides of America or Australia. These reactions have been proved on the large or ton scale, and there is no technical difficulty. Unfortunately mine people are somewhat ignorant of electrical matters, and it is exceedingly difficult to get them to understand or appreciate a process like this, capable though it may be of paying good dividends on very large capitals indeed.

"In all these metallurgical extractions we may roughly take the cost of energy as a farthing per kilowatt hour for steam, and half that for gas. Allowing a rough average pressure per cell, we may take it that electric energy costs $500 per ton, or ton equivalent by steam, and $250 by gas. That would be $15 a ton for zinc, $5 for lead, $15 for copper and iron by steam, and half these figures by gas-power. This means that the metallurgy of all sulphides, except, perhaps, iron, is within our grasp. It may pay to make a pure iron, free from phosphorus, silicon, manganese and carbon at something under $50 a ton from pyrites ores (which may also contain zinc, nickel, copper, etc.), and then, add exactly the desired amount of other constituents or 'physic' to produce with accuracy steels of special grades.

"But our limit in electrolysis in this country [England] is almost entirely human inertia. Commercial and financial people do not understand it, and fight shy of it. But our technical people are nearly as bad. The pure physicist, as a rule, takes no interest in electrolysis or physical chemistry, and thinks it belongs to the chemical class room on the other side of the passage. The chemist thinks it is higher mathematics, and will have none of it; the mathematician thinks it may be an exercise in differential equations; but they are all agreed that it is a sort of continental fungus which flourishes with no roots, and that it is beneath the attention of a scientific man to know enough about it to give a reason for the broad statement that it is all nonsense."

* See *Electrochemical Industry*, Dec., 1902, vol. I, page 118.

ELECTROLYTIC REFINING OF GOLD.

By D. K. TUTTLE, PH.D.
Melter and Refiner, U. S. Mint, Philadelphia

The problem of refining silver containing small amounts of gold, and other impurities, by electrolysis has been solved, and the industrial establishments of to-day treat practically the entire silver product of our mines in this manner.

Only the gold residues reach the mints. Indeed, the scarcity of silver deposits at the Government institutions has been a serious inconvenience, since the usual acid-refining methods require a large amount of that metal as parting material in treating the gold bullion received.

The great mass of gold deposits contain some silver and are usually too impure for either coinage or industrial use without refining. Some contain platinum, which is lost in the usual wet processes.

It has been the practice to alloy the gold in the deposits with 2⅓ times its weight of silver, and subject this mixture to the action of nitric or sulphuric acid. In consequence of the very limited deposits of silver, it is necessary to use the same silver repeatedly as parting material, at a great expense for acid. If 2½ times as much impure silver as of gold came to the mints, the parting processes would not be so wasteful.

The only process for directly refining gold electrolytically that is known to have been reduced to practice is that patented by Dr. Emil Wohlwill, Hamburg, Germany, United States patents 625,863 and 625,864.

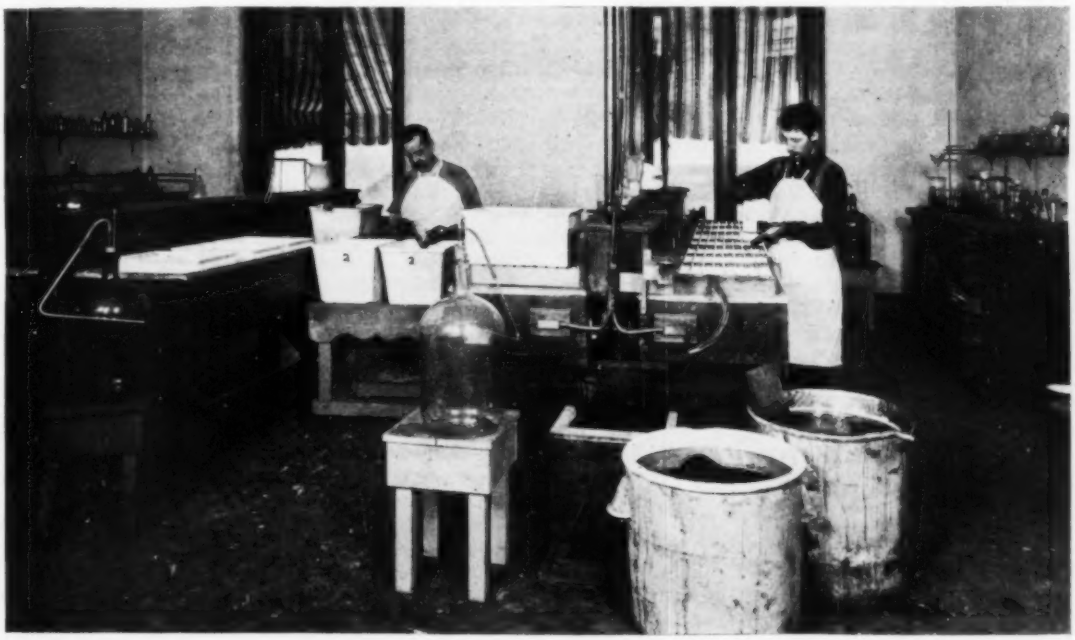
The feature protected by patent is the electrolyte. This is composed of gold chloride solution rather strongly impregnated with free hydrochloric acid, and it is in this latter point that the significance of the invention lies. If a gold anode be placed in a neutral or only slightly-acid solution of gold chloride, opposed by a suitable cathode, gold will be deposited by an electric current, but little or no gold will be dissolved from the anode. Free chlorine is given off; a result not to have been anticipated since chlorine is an active solvent for gold. Upon the addition of free hydrochloric acid to the bath, a point is reached where the chlorine at the anode is suppressed, and gold passes into solution, equivalent for equivalent, to that deposited. The strength of the electrolyte is easily maintained by such additions of gold chloride from time to time as will be equivalent to the copper, platinum, etc., dissolved from the anode, and not deposited on the cathode. The operation is continuous until the solution becomes highly charged with impurities.

The Wohlwill process is in use in the two great refineries of Germany—the North German at Hamburg and that at Frankfurt (formerly Dr. Rössler). In a private letter to the writer, Dr. Wohlwill states that gold has been refined by electrolysis in the Hamburg plant since 1878, uninterruptedly, and that now practically all the gold refining done in Germany is effected by this method.

Correspondence with the patentee resulted in the purchase of a right to use the Wohlwill patent in the mint at Philadelphia, and a plant has been introduced which is being gradually enlarged.

PROCESS.

The apparatus consists of first: A dynamo, which, when run at its normal capacity, requires 5 horse-power and furnishes a current of 600 ampères at 6 volts. The machine having been designed with a view to experimental work, a rheostat in the field-winding enables us to regulate the current between 100 and 600 ampères.



ELECTROLYTIC REFINING ROOM, U. S. MINT, PHILADELPHIA.

Second: The cells, which are of white porcelain (Berlin ware), are 15 inches long x 11 inches wide and 8 inches deep. These are filled with a prepared solution of gold tri-chloride containing 30 grammes of gold per litre (3 8-10 Troy ounces per gallon), the depth of the solution being such as not to entirely submerge the anodes. In each of these cells are suspended 12 anodes and 13 cathodes, *in multiple*. The anodes are each 6 inches in length, 3 inches wide and ½ inch thick. The corresponding cathodes are of fine gold and rolled down to 1-100 of an inch in thickness. The distance between anode and cathode is 1½ inches. In our present working seven cells are placed end to end on a bed of sand, underlying which is a series of steam pipes by which the temperature of the bath may be raised and maintained at any desired degree. At present our cells are kept at from 50° to 55° C. The increased temperature serves to reduce the voltage required, and at the same time to diminish the amount of free acid necessary to suppress evolution of chlorine at the anodes.

Circulation of the electrolyte by mechanical means is necessary to secure uniform disintegration of the anode and deposition of the gold.

The seven cells in use are connected up, *in series*, with the dynamo, which is at present regulated to furnish 100 ampères. The tension between the terminals of the seven cells varies from 4½ to 5 volts, dependent upon temperature, strength of solution, etc.

The chemical equivalent of gold is very high, and the electromotive force required for the deposition of gold is very low, so that the power necessary for running the plant is insignificant. With only seven cells of our plant in operation, we are refining about 5,000 ounces per week, with the expenditure of about 1 horse-power. One attendant suffices to manage the work, with the occasional assistance of a second workman.

The cost for hydrochloric acid in the bath is 20 cents per 1,000 ounces of deposited gold.

We can increase our refining capacity to 50,000 ounces per week with our present plant.

Beside the advantage the process offers for the refining of gold with an insignificant consumption of acid, with little labor, and small expenditure of power, an important one should be mentioned, viz., the recovery of any platinum present in the bullion. This dissolves, but is not deposited with the gold. When the electrolyte becomes sufficiently charged with platinum, the gold is first precipitated by sulphur dioxide, and removed. Then the platinum remaining in solution is separated as ammonium platinum chloride. Lastly, the copper is recovered by passing the wash waters over iron scrap.

With these advantages to its credit, the process has limitations which are serious ones. Any silver in the anodes will, of course, be converted into insoluble chloride, and if the percentage be small will fall to the bottom of the containing tank as "slimes." But if the amount of silver exceed 5 per cent. the chloride tends to adhere to the anode, as a crust, which must be mechanically removed.

Furthermore, any considerable quantity of copper present in the bullion to be treated is undesirable, since the electrolyte, in that case, must be renewed inconveniently often.

There seems to be reason to think that any electrolytic process for parting and refining gold will not have the same success in this country in our industrial plants as it met in Europe. The Australian, South African and Hong Kong native gold is very much purer than even our California nuggets, and they were very much better than our recent finds in Alaska.

Hong Kong gold is reported as containing .975 gold, .020 silver, .0005 platinum, .0005 iridium.

Some recent consignments of Klondike gold to this mint varied from .776 gold to .834 gold, .219 silver to .161 silver, with no showing of platinum or iridium in the electrolyte.

Such bullion can only be successfully treated by the "Wohlwill" process when blended with a higher-grade gold. We prefer not to treat bullion having a fineness of less than .940 gold.

Again, the Government conditions for the gold producer here are much more favorable than in other countries. At any United States mint or assay office the depositor is entitled to receive promptly upon assay of his bullion all the gold it contains in the form of gold coin or draft on the treasury, less some slight charges. If the amount of the deposit be large he may even receive an advance of 80 per cent. on its approximate value at the time of making the deposit. Under these circumstances the question of *interest* becomes an important item with the industrial establishments. With a given output per diem, several times the value will be locked up in solution, anodes, cathodes and material in various stages of leaching, melting, etc.

It is to be feared that with the liberal system in vogue in this country, the depositor will still find it to his advantage to deliver to the Government high-grade, but not very pure, bullion for spot cash, pay the slight charges and leave the melter and refiner to wrestle with the refining.

For the patrons of the United States mint, however, the "Wohlwill" process has been a great boon. The gold bars furnished have been exceptionaly high (999.8), and this grade is especially sought by makers of dental gold and leaf. Under slight pressure it coheres and compacts into a reguline mass, as perfect as if melted and poured in a mould. A medallion head of Washington was made from spongy electrolytic gold by simple pressure in the die press, and the result was a perfect success, too soft for wear, but a beautiful medal.

This especially high-grade gold is being distributed to appreciative customers at many points distant from Philadelphia.

THE PRESENT METALLURGY OF ALUMINIUM.

By Joseph W. Richards, Ph.D.

President of the American Electrochemical Society.

THE aluminium now being manufactured is being made by one process only, viz., the electrolysis of alumina dissolved in a bath of melted aluminium-sodium double fluoride. The principle involved in this process was discovered by Paul L. V. Hèroult, in France, and Charles M. Hall, in the United States, in 1886. The principle is easily understood when once known; it is, that the melted double fluorides of aluminium and more electropositive metals can dissolve a considerable proportion of their weight of the relatively infusible alumina, and that when such a solution is electrolyzed, aluminium and oxygen appear at the two electrodes until the dissolved alumina has been almost entirely eliminated; and that, by the addition of fresh alumina the process can be made continuous, while the solvent bath material remains unaffected by the operation.

Before describing the efforts of Hall and Hèroult, it may be well to say that the process is the invention of these two investigators alone, and the hysterical attempts of Mr. A. Minet to claim a share in the discovery and application of this principle, especially his temerity in calling the present process the Minet-Hall process, are without the slightest basis or justification in actual fact. In a recent German monograph, Mr. Minet devotes 19 *lines* to the original patent of Mr. Hèroult (by which some 3,000 tons of aluminium is manufactured yearly), 32 *lines* to the patents of Hall (by which some 6,000 tons is made yearly), and *20 pages* to the description of Minet's process, by which not a pound is being commercially manufactured, nor is it at all likely to be. Hall's and Hèroult's processes were discovered, and patents applied for, in 1886; Minet himself dates his first experiments from February, 1887. Minet makes a bath of 60 parts sodium chloride and 40 parts aluminium-sodium chloride or fluoride, and electrolyses this bath, producing therefrom aluminium and chlorine, or perhaps, fluorine, and regenerates the bath by piling alumina around the anode where, by the simultaneous contact with the carbon anode and the gaseous halogen, it is partly decomposed and enters the bath as aluminium fluoride. Such, at least, is what Mr. Minet says happened to his bath; but, however that may be, no sodium chloride is used at all in the present process of manufacture, and while Minet may make a Quixotic claim that the present is the Minet-Hall process, no court would sustain his claim, particularly since he only began his experiments the year *after* Hall and Hèroult had applied for their patents.

Turning now to the Hèroult process, it was first conceived by him in 1886. At the Metallurgical Congress at Paris, in 1900, Hèroult described how he stumbled across it. He was attempting to electrolyze melted cryolite, the native double fluoride of aluminium and sodium, $AlF_3.3NaF$, with an iron cathode and carbon anode, and adding some double chloride of aluminium and sodium, $AlCl_3.2NaCl$, to the melt to make it more easily fusible. He obtained aluminium alloyed with his iron cathode, but no evolution of either chlorine or fluorine at the anode, yet the anode was attacked and evolved a gas. He concluded that some oxide had gotten into the bath, whose

oxygen was attacking his anode. He took up this clue, and on testing the aluminium-sodium double chloride which he had used, found that it had been largely converted into alumina by the moisture of the air, and thus alumina had gotten accidentally into the bath. On adding pure alumina, later, he found that this explained the question, and that the electrolysis produced only aluminium and carbonic oxide.

Hèroult was then a student, twenty-three years old, and after taking out his patent in France in April 23, 1886, number 175,711, he went for advice to the established manufacturer of aluminium by the sodium process—Pechiney at Salindres. Here he was advised that the uses of pure aluminium were so limited that his process was of little value, and that if he would put his attention on producing cheaply the alloys of aluminium and copper or iron he would start a much greater industry. He accordingly set to work on his idea of electrolyzing pure alumina melted alone in the electric furnace, using a copper or iron cathode, and in 1887 took out additional patents for this alloy process. Going thence to Switzerland, he worked for a year at the Rhine Falls, producing only aluminium alloys, such as the bronze, by this alloy process. Finding in 1888 that Hall, in America, was producing commercially pure aluminium by a process analogous in principle to his original patent, Hèroult resurrected his earlier pure-metal process and, with the aid of Dr. Kiliani, set to work making pure aluminium, which he placed upon the market only some twelve months after Hall in America had commenced operations on a commercial scale.

The process of Hèroult, patented in 1886, describes putting alumina into a carbon crucible, and adding cryolite in sufficient quantity to render it fluid at a moderate heat. The crucible itself serves as cathode while a carbon anode dips into the bath. The crucible is placed inside a larger graphite crucible, and the space between the two filled with graphite, into which dips the negative carbon. A cover having holes for the insertion of the conducting carbons is provided, and a layer of clay or loam put on top to exclude air and gases. Hèroult stated that a current of three volts was sufficient to produce decomposition, but that a convenient strength of current for a crucible 20 centimeters deep by 14 centimeters inside diameter, with a carbon anode 5 centimeters in diameter, was 400 ampères, which required a potential of 20 to 25 volts. The crucibles were placed in a wind furnace and kept hot by a fire, during the electrolysis. The idea of a continuous operation by adding fresh alumina is conspicuous for its absence in this description, as all the arrangements point to the idea of running a charge in the crucible, tightly closed, then lifting it out of the furnace, removing the luting and covers, and removing the contents of the crucible.

The probabilities are that Hèroult did not make more than a few ounces of metal in this way until 1889, when, hearing of the success of Hall in America, he started, with Dr. Kiliani's assistance, to develop his process into commercial shape, and it was not until September, 1890, that his company was selling pure aluminium.

How the process has been developed abroad we know only by the results. Dr. Kiliani patented a revolving furnace, with a movable anode, but this has been abandoned. The European Works, operating under Hèroult's patent, are not open to the public, and no details of their working are given by the managers. It is the writer's opinion that the method of working adopted in these works is practically that used by Hall in America since 1888, and that the great secrecy of the European makers is used principally to avoid it being known how closely they have copied the American style of apparatus. This opinion may be wrong, but it explains the situation so well that it commends itself as the true reason of their secrecy.

The plants working with licenses under the Hèroult patents are the Aluminium-Industrie-Aktien-Gesellschaft, at Neuhausen, Switzerland, 4,500 horse-power; at Rheinfelden, Baden, 5,000 horse-power, and at Lend-Gastein, near Salzburg, Austria, 3,000 horse-power; also the Société Electrometallurgique Française at La Praz, Savoy, 3,000 horse-power, and the British Aluminium Co., at Foyers, Scotland, 6,000 horse-power. Part of the power of all of these plants is used for making calcium carbide, and the proportion used for aluminium is not exactly known; it is probably not over 12,000 horse-power in all of those plants put together, and possibly less.

Mr. C. M. Hall approached the subject from the standpoint of trying to find a fluid melted salt in which alumina would dissolve and out of which it could be electrolyzed. As he has several times explained to the writer, he had in mind the analogy to dissolving a salt, such as copper sulphate, in water, and obtaining the ingredients of the salt at the two electrodes without decomposition of the water. For this end, he experimented to find a melted salt which would (1) dissolve alumina freely, (2) conduct electricity, (3) yield only aluminium and oxygen on being electrolyzed, (4) not volatilize or deteriorate on continued use. After a long and arduous investigation, in which almost all the single and double salts of aluminium were tested, and many fusible salts of other metals, Mr. Hall discovered that the double fluorides of aluminium and the more electropositive metals were the only salts which possessed the above qualifications. The process was first operated in February, 1886, and patents applied for July 9th of the same year.

During this period, in May, 1886, Mr. Hèroult, of France, had applied for a United States patent corresponding to his pure-metal process, already described. The patent office instituted interference proceedings, with the result that it was found that Mr. Hall had made his invention and practised it before any publication of Mr. Hèroult's process had been made, and was, therefore, entitled to the United States patent. In consequence of this decision the patent in this country was issued only to Mr. Hall. Later, Hèroult obtained United States patents for his alloy process, and the same was installed experimentally at Boonton, N. J., but it was not a commercial success.

Mr. Hall applied on July 9, 1886, for a single patent, which was issued on April 2, 1889, after division of the original application and re-application. The patents are numbered 400,664, 400,665, 400,666, 400,667 and 400,766. They cover variations of the original principle. For instance, Mr. Hall found that the double fluoride of aluminium and potassium or lithium was a very easily fusible salt, and possessed the required qualifications for use in his process, being of particularly low specific gravity. The cost of these salts is the particular item in which they are inferior to the corresponding sodium salt. Again, the double fluorides of aluminium and the alkaline earth metals are also effective, with the drawback of a high specific gravity, greater than that of aluminium, and therefore more suitable for producing alloys of aluminium than the pure metal.

Two of the broadest claims of Mr. Hall are as follows, from patent number 400,766:

"1. As an improvement in the art of manufacturing aluminium, the herein-described process, which consists in dissolving alumina in a fused bath composed of the fluorides of aluminium and of a metal more electropositive than aluminium, and then passing an electric current through the fused mass, substantially as set forth.

"2. As an improvement in the art of manufacturing aluminium, the herein-described process, which consists in dissolving alumina in a fused bath composed of the fluorides of aluminium and sodium, and then passing an electric current, by means of a carbonaceous anode, through the fused mass, substantially as set forth."

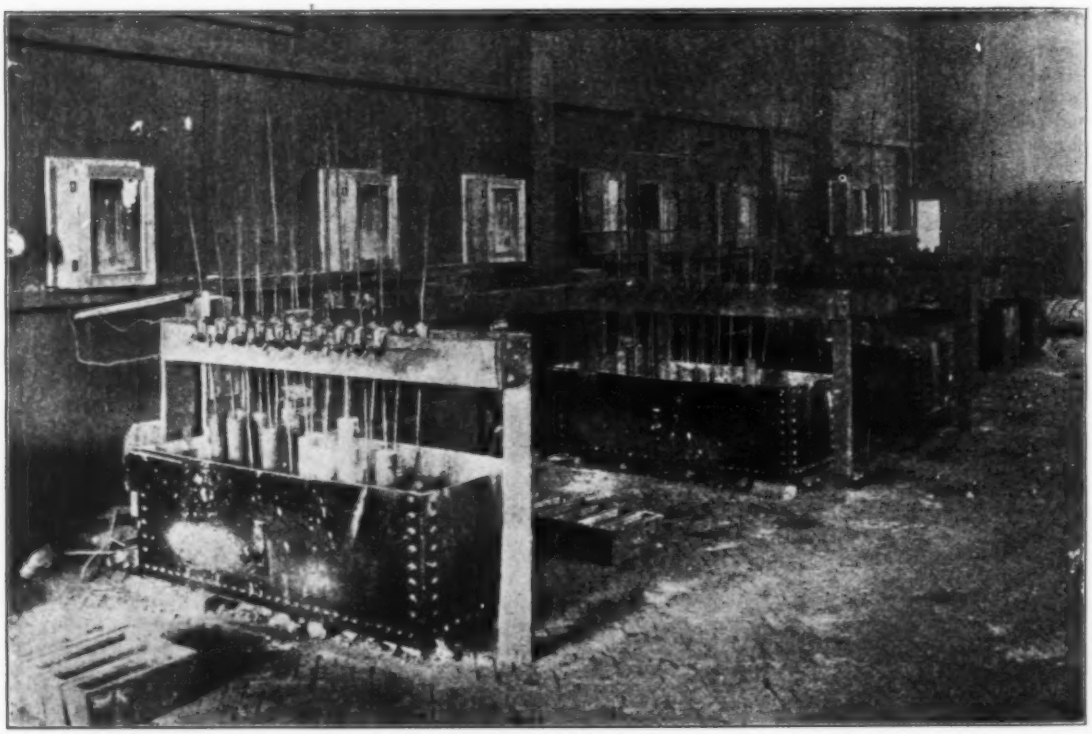
The other patents enumerated claim specifically the use of double fluoride of aluminium and potassium to form the bath, also of lithium fluoride in the bath in place of part of the sodium or potassium fluoride, also the use of calcium fluoride in the bath, and of the double fluorides of aluminium and

alkaline-earth metals. In patent 400,667 especial emphasis is laid on preserving the continuity of the operation by adding alumina as the bath becomes impoverished in alumina, and removing aluminium from the bath, by tapping or ladling out, without interrupting the process.

The Hall process first began commercial operations at Pittsburg, using 125 horse-power, in November, 1888, and producing 50 pounds per day. Since then, the history of the process is one of steady increase in size and efficiency. In place of small cast-iron pots, taking 1,800 ampères and requiring 8 volts to run them, and requiring over 2 horse-power to each pound of aluminium produced daily, there are now used large wrought-iron pots, taking 10,000 ampères and requiring but 5 to 6 volts each, and producing probably 1½ pounds of aluminium daily for each horse-power applied. In place of the 125 horse-power at Pittsburg, there is now in use 10,500 horse-power at Niagara Falls and 5,000 horse-power at Shawinegan Falls, Quebec.

The principle of the process, however, retains its original simplicity. The bath material consists of the double fluoride of aluminium and sodium; alumina is dissolved in this up to a maximum of 15 to 20 per cent. As the alumina is removed by electrolysis and the resistance of the bath goes up, fresh alumina is stirred in. The 3-inch carbons used carry each 250 ampères of current, and are kept at approximately an inch from the negative electrode, which is the melted metal in the bottom of the pot. The large size of the pot and correspondingly heavy ampèrage passing through develops enough heat in the electrolyte to keep the contents melted without the assistance of exterior heating, which is thus rendered unnecessary by the scale of the operation. The metal formed sinks in the bath because its specific gravity, melted, is 2.54, while that of the bath varies between 2 and 2.35, at most. The temperature of the operation is 900° C. (1,650° F.). One bath will continue in uninterrupted operation several months, the carbon anodes being renewed as they burn away, which they do at the rate of 1 pound of anode per pound of metal produced.

All the impurities of the alumina used pass into the metal produced, and to obtain pure metal it is therefore absolutely necessary to use the purest alumina. This requirement has led to considerable improvement in the manufacture of alumina, the Baeyer process being in considerable use both here and abroad, while in addition to this, Mr. Hall has invented a lime-process of wet chemical treatment, which is installed on a large scale at East St. Louis and is producing alumina of the highest quality; he has also patented the method of purifying bauxite or crude alumina by mixing it with sufficient reducing agent to reduce the impurities present, and then melting down the mixture in an electric furnace. The result of the last process is a dense, granular purified alumina, in form and composition very suitable for reduction. The lime process is the subject of Hall's United States patent 663,167 of December 4, 1900; while the electric-furnace method of purification is in United States patents 677,208 and 677,209 of June 25, 1901, and 706,553 of August 12, 1902. The Pittsburg Reduction Co., operating the Hall process, also bakes its own carbon electrodes by an electric-furnace process described in Hall's United States patent 705,076 of July 22, 1902.



A HALL ALUMINIUM BATH.

The commercial production of aluminium in America is, therefore, wholly by the application of Hall's process of electrolytic reduction, supplemented by Hall's lime or electric-furnace process of purifying alumina and the same inventor's process of baking carbon electrodes. It was not the purpose of this article, however, to enter into detail on the commercial side of the production of aluminium, and we will conclude by discussing the reactions taking place in the process, *i. e.*, by regarding the scientific aspect of the process.

First, as to the facts. Cryolite, the sodium-aluminium double-fluoride, melts at 800° C. When melted, it is transparent and one can see through several inches of it to the bottom of the vessel containing it. If powdered alumina is stirred into it, it largely dissolves at once, without ebullition or evolution of heat or any signs of chemical action. If a large amount is added at once, some will be seen at the bottom

of the melt gradually dissolving and disappearing. About 20 per cent. of the weight of the bath can be thus taken up, and the bath remains homogeneous; if over 25 per cent. is added some remains undissolved at the bottom. Neither the bath material alone or the solution containing alumina wets, *i. e.*, adheres to, carbon. Carbon rods or even powdered carbon stirred into the bath, rise to the surface and emerge without the bath material sticking to them. On passing a direct electrolytic current through this bath aluminium appears at the cathode, and oxygen at the anode. If the anode is of carbon, carbonic oxide is there evolved; if it is of bright copper, a skin of cuprous oxide first forms on it, and afterwards oxygen is evolved. If the alumina in the bath is allowed to become exhausted, fluorine commences to evolve at the anode; if a very high current density is used sodium vapor shows itself at the cathode. The working temperature of the bath is 900° to 950° C., and its specific resistance is about 3 ohms per centimeter cube.

Mr. Adolphe Minet has made a number of measurements of the resistance and electromotive force required for decomposition in baths containing 60 per cent. of sodium chloride, and it is, therefore, not at all certain that his conclusions apply to the present manner of manufacturing aluminium. He concludes that in a bath containing sodium fluoride, sodium chloride and aluminium fluoride, mixed together, the aluminium fluoride must be decomposed, because it is the weakest of the three salts, and the salt thus removed may be returned to the bath by piling alumina around the anode where it may be converted into fluoride by the evolved fluorine. He claims that when alumina is added to such a bath it does not dissolve, but remains mechanically suspended, and so regenerates aluminium fluoride by being decomposed by the fluorine evolved at the anode. As stated above, the presence of an excess of sodium chloride vitiate all Minet's conclusions, as applicable to Hèroult's and Hall's processes, and, furthermore, all the phenomena of the electrolysis of Hall's and Hèroult's baths point to a different explanation.

Hèroult himself advanced the even less plausible theory that sodium was primarily evolved at the cathode and fluorine at the anode, that the sodium then acted upon the aluminium in the electrolyte as aluminium fluoride and reduced out its metal, while the fluorine at the anode acted upon the alumina suspended (not dissolved) in the melt, and set free its oxygen, forming aluminium fluoride. This theory is such a maze of contradictions as to be indefensible. Primarily, the disappearance of alumina stirred into the bath is proof of its becoming incorporated into the electrolyte, and any electric current passing through would separate aluminium at the cathode in preference to the more positive sodium. The theory of Hèroult, unsustained by any experimental proofs to establish his position, is certainly untenable.

In the writer's opinion, and from his repeated observation of the process and experimenting with it in various ways, the conclusion of Mr. Hall that he really has a solution of alumina in a fluid bath analogous to a salt dissolved in water, is the best explanation of the facts. The alumina dissolves apparently like sugar disappearing in water, without ebullition, evolution of gas or heat, or any appearance of chemical action. If the result is an oxyfluoride bath, as some think, it may be well to note that an oxyfluoride is merely a combination of Al^2O^3 and Al^2F^6, and the union, if it exists at all, is chemically a very weak one. When a salt goes into solution in water, the hydrate theory of solution assumes the existence of possible combinations of salt and water in the solution, but of such a weak character of combination as to practically be negligible as compounds. With these facts in mind, it appears that the statement of Mr. Hall that his alumina *goes into solution* in the bath is a very exact statement of the phenomenon.

As concerns the decomposition of the bath, everyone who has worked with the process knows that aluminium appears at the cathode and oxygen at the anode. The most evident inference is that the alumina in solution is decomposed, and its constituents appear at the electrodes. Anyone who would maintain that the primary electrolysis proceeds otherwise and that one or both of these products are secondarily produced, must certainly shoulder the burden of proof to support his view. But, when we come to analyze the reaction, and discuss the probability of secondary reactions occurring, we find the probabilities all in favor of the decomposition into aluminium and oxygen being primary.

There are present in the bath, or, at least, go into its composition, sodium fluoride, aluminium fluoride and alumina. The heats of formation and voltages thoretically necessary for decomposition of these salts are as follows:

Sodium fluoride (Na, F) = 109,700 calories, requiring 4.7 volts.

Aluminium fluoride (Al, F^3) = 296,000 calories, requiring 4.0 volts.

Aluminium oxide (Al^2, O^3) = 392,600 calories, requiring 2.8 volts.

With these substances going into the composition of the bath there is not the slightest doubt but that aluminium and oxygen should be primarily separated out at the electrodes on passing the current. The facts are that these products do appear, and the burden of proof is certainly on anyone who would maintain that the reaction is in any way different from the above. If a carbon anode is used, carbonic oxide appears, and only traces of carbon fluoride; if copper is used, it coats itself with oxide, not with fluoride, and afterwards pure oxygen is evolved. The writer cannot understand how anyone can doubt the primary evolution of oxygen and aluminium from the bath, if they are acquainted with the details of the process and its mode of working.

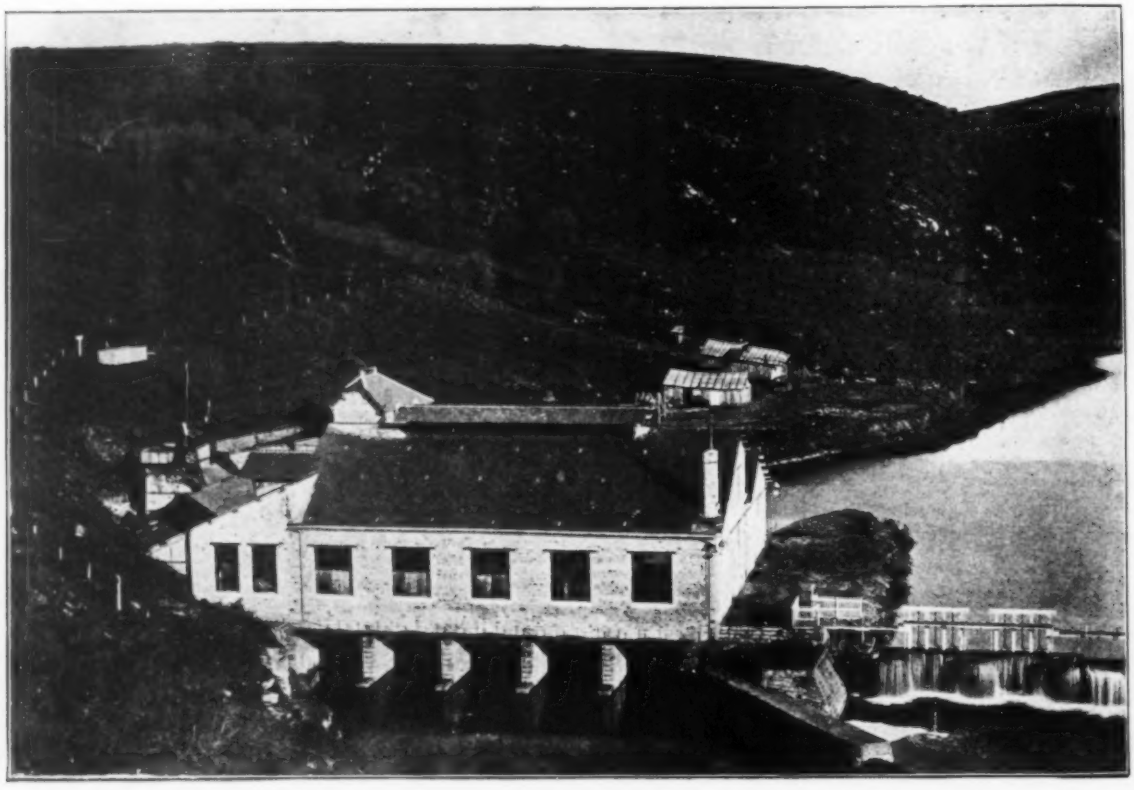
Haber and Geipert published in the *Zeitschrift für Elektrochemie* for 2d and 7th January, 1902, the results of some laboratory tests of this process on a rather large scale, using a current up to 400 ampères. They obtained about 50 per cent. of the theoretical output, and remark that the electrolysis of this solution of alumina proceeds as quietly and regularly as an analytical determination in aqueous solution. They determined to their complete satisfaction that only traces of carbon fluorides were evolved during the electrolysis, and that the bath will not take up uniformly above 20 per cent. of its weight of alumina. With their small apparatus they found a current density of 3 ampères per square centimeter of floor surface kept the bath fluid, while in large manufacture one-third that much suffices. The difference is due entirely to working with 400 ampères or several thousand. They used a working voltage of 8.5, whereas on a large scale only two-thirds that voltage is necessary, using the lower current density.

Prof. J. W. Langley has recently given, in the "Transactions of the American Electrochemical Society," Vol. II, page 260, the results of measurements of the counter-electromotive force in electrolyzing alumina dissolved in melted cryolite at 1,010° C., using 1,000 ampères of current. The measurements were only approximate, but showed a counter-force rising to 1.22 volts during continuous electrolysis by 5 to 10 volts applied. This is not the disruptive work of the current, but, as Prof. Langley happily phrases it, is "the instantaneous value of the counter-electromotive force existing *during the passage of the current.*" It is very probably the measure of the tendency of metallic aluminium to decompose the carbonic oxide gas at the anode and form the lowest oxide of aluminium. But, the current is decomposing the highest oxide of aluminium, and, therefore, the voltage absorbed in decomposition is higher than the counter-electromotive force.

The writer has satisfied himself, from measurements of the current in ampères passing through the bath, using different potentials, that the chemical work being done by the current is represented by nearly 2.2 volts, which corresponds to the decomposition of alumina (2.8 volts) minus the energy furnished by the oxidation of the carbon (0.6 volts). Prof. Lang-

ley's determination of the counter-electromotive force being 1.22 volts is not inconsistent with this; it simply means that if the current is suddenly thrown off, the ions at the electrodes do not tend again to form alumina and carbon, but sub-oxide and carbon, with a total energy evolution measured by 1.22 volts.

It is a pity that a process of such beautiful simplicity, theoretical interest and commercial importance has not been more closely studied, and more definitely described. Commercial reasons have doubtless actuated the workers of the process in keeping all its details as secret as possible, but it is to be hoped that the awakening of electrochemical industries which has taken place in the last year or two will soon touch this field, and help us to fill some of the gaps in the scientific understanding of this process. The writer is convinced that a clearer understanding of the modus operandi of this process would undoubtedly lead to fruitful results in the application of similar principles to the extraction of some of the other electropositive metals.



KERROUSSE PLANT.

A FRENCH PLANT FOR MAKING STEEL IN THE ELECTRIC FURNACE.

In Europe, France may be considered to be the country par excellence of water-power development. Especially in the French Alps a great number of hydro-electric stations were erected in recent years, and a remarkable rise of electrochemical industries took place in connection with this development. As the possession and development of a water-power in France is governed by certain laws, this industrial development was somewhat influenced by legal restrictions. To thoroughly discuss the legal and the industrial aspect of the case, all those interested in water-power development in France, united last fall at Grenoble in the "Congrès de la Houille Blanche," *i. e.*, in literal translation, "White Coal Congress," attributing the poetical name "white coal" to the white snow mountains with their waterfalls, available for generating power.

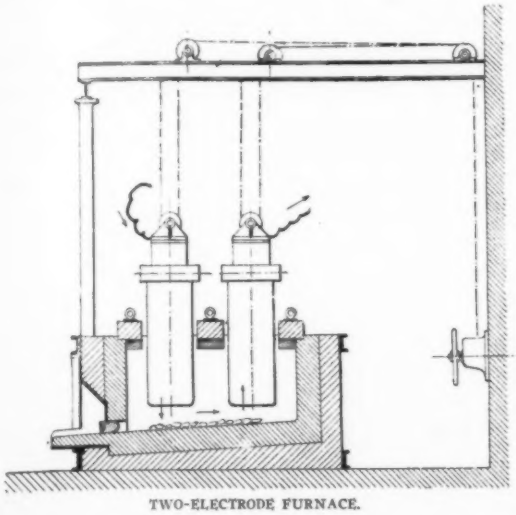
Among the papers read at the congress was one of special interest, as it dealt with an entirely new electrochemical industry. Its author was Mr. Charles Bertolus, electrometallurgist at Saint-Etienne (Loire); and the subject of the paper was the manufacture of different kinds of steel in the electric furnace in the Kerrousse plant of Keller, Leleux & Co. For a copy of the paper, as well as for the cuts and for some valuable additional notes, we are indebted to Mr. P. McN. Bennie, European manager of the International Acheson Graphite Co.

The plant at Kerrousse, near Hennebont (Morbihan), was erected by Keller, Leleux & Co. for the purpose of manufacturing calcium carbide; but when it was nearly completed, the French courts handed down a decision awarding to Mr. Bullier all patent rights to make calcium carbide in France, so that the plant at Kerrousse was prevented from starting the manufacture of carbide. As the apparatus for electrometallurgical operation had been installed, it was decided to utilize the plant partly for the manufacture of ferro-alloys and partly for making steel in the electric furnace. The latter process is described in the paper of Mr. Bertolus.

The plant at Kerrousse utilizes a waterfall of the river Blavet of about 550 horse-power. There are four vertical turbines each of 135 horse-power, coupled at will to a horizontal shaft driving two alternators of 200 kilowatts each, and two exciters. The alternators are designed to give current at three different voltages, according to the external circuit to which they are connected, and according to the special electrometallurgical process for which the current is used.

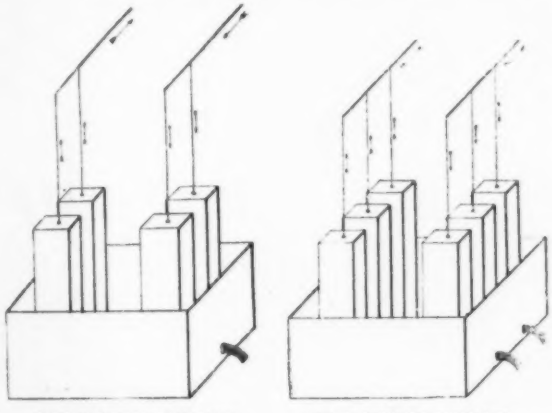
The furnace room is divided into two parts: one-half contains four electric furnaces for making ferro-alloys, the other half special electric furnaces for treating iron ores and making steel.

Mr. Keller, a member of the firm which owns the plant, obtained his first satisfactory results in the treatment of iron with his "two-electrode furnace. This furnace contains two vertical electrodes, placed side by side; the furnace has walls of brick and a refactory bottom. At each electrode a distinct



TWO-ELECTRODE FURNACE.

zone of high temperature is produced, and these two high temperature zones are in series with the fused or partly fused materials between them. Either high temperature zone may be separately regulated, by a simple movement of the electrodes. This two-electrode furnace has, however, two dis-



FOUR-ELECTRODE FURNACE. SIX-ELECTRODE FURNACE.

advantages: the capacity of the furnace is limited and the continuity of operation is interrupted whenever an electrode is to be renewed. These disadvantages are successfully overcome by using four or six or more electrodes, one-half of the electrodes being connected to the positive pole of the circuit, the other to the negative pole. It is evident that with this arrangement there is practically no limit of the dimensions of the furnace, and that a single electrode can be replaced without interrupting the whole operation.

In his first experiments Mr. Keller used the same apparatus for the reduction of the iron ore and for the subsequent conversion into steel. There was the disadvantage that both steps require different treatment. To enable economical reduction of the iron ores, the furnace must be able to accommodate a considerable quantity of the materials to be treated; on the other hand, for refining purposes a rather shallow furnace is required with the material held in a condition of perfect fluidity and easily accessible. These reasons lead to the adoption of two electric furnaces "en cascade" (in tandem), the upper furnace being intended for the reduction of the iron ores, and the lower furnace for the subsequent refining and purification process. As each furnace serves a special purpose, it is designed to meet the special demands of this purpose. This is the arrangement of the 375 horse-power furnace which we will describe later. It may be mentioned that Mr. Bertolus in his French paper always speaks of the "haut-fourneau électrique." Mr. P. McN. Bennie remarks that a new name seems necessary for this type in English; it might be translated as blast furnace, because the general appearance is that of the ordinary blast furnace, although in the electric furnace there is no "blast."

The upper furnace has four electrodes; the bottom is inclined towards the tapping hole. Above the fusion chamber of the furnace there is a column made of brick, and into this shaft the ores, the carbon for reduction, and the fluxes are fed. Below the tapping hole of the upper furnace, the lower furnace is placed which receives the cast iron; it can be closed by removable covers of refactory material and is provided with two electrodes the position of which is adjusted by hand.

When the operation begins, the materials to be treated are fed into the shaft at the top of the furnace. In order to observe the condition of the separate high temperature zones at the end of each of the four electrodes, four ammeters are provided, one in the circuit of each electrode, and two voltmeters; the regulation is then accomplished by a movement of the electrodes. The fusion and reduction of the ore starts at the bottom of the furnaces. The gases developed rise to the upper part of the furnace and are then burned in a suitable chamber, in order to utilize the heat for drying fresh material to be fed into the furnace.

After several hours, the molten metal is drawn off into the lower furnace which has been previously heated and already contains fused materials. When the metal has been drawn off from the upper furnace down to the slag, the tapping hole is closed, and new material is fed at the top into the upper furnace. After a certain time the slag of the upper furnace is discharged through an opening provided for this purpose in the side of the furnace. The slag and the metal are examined at regular intervals, and it is possible to obtain a metal of absolutely uniform composition.

When the lower furnace contains a sufficient quantity of liquid metal, the process of refining is started; the current is so adjusted as to accomplish perfect liquidation and rapid reaction of the metal with the refining and purifying agents.

Mr. Bertolus remarks that the rough metal may be decarburized either by adding oxide to the bath, the oxide added being the iron ore itself, or by the addition of scrap iron. The purification is brought about by a suitable addition of lime. Samples are taken at regular intervals, to determine the stopping point of the process of decarburizing and purification. The further treatment seems to be the same as in the ordinary metallurgical process.

Mr. Keller, who is personally in charge of this process, remarks that on account of the relatively small amount of power at this point, it was not thought to be advisable to install certain additional improved apparatus deviced by him for the manufacture on a large scale. He claims that his new apparatus would enable him to cast and refine quantities of steel of 15 to 20 tons at the same time, or even more if necessary. Mr. Bertolus states that he was also present when the process of making steel from scrap iron was worked; this process requires somewhat different electrical conditions.

The principal point is, of course, the cost of the process, and for this reason we give herewith a literal translation in full of the portion of Mr. Bertolus' paper, dealing with the cost of the process. The figures given are, of course, based upon the conditions in France; we have changed the figures from French into American money, 5 francs being assumed to be one dollar.

"We have verified that the manufacture of one ton of steel

requires 2,800 effective kilowatt hours, say, about 3,800 electric horse-power hours. To determine the cost in the case of the direct treatment of the ore, we assume as a basis the following prices which are taken from ordinary practice:

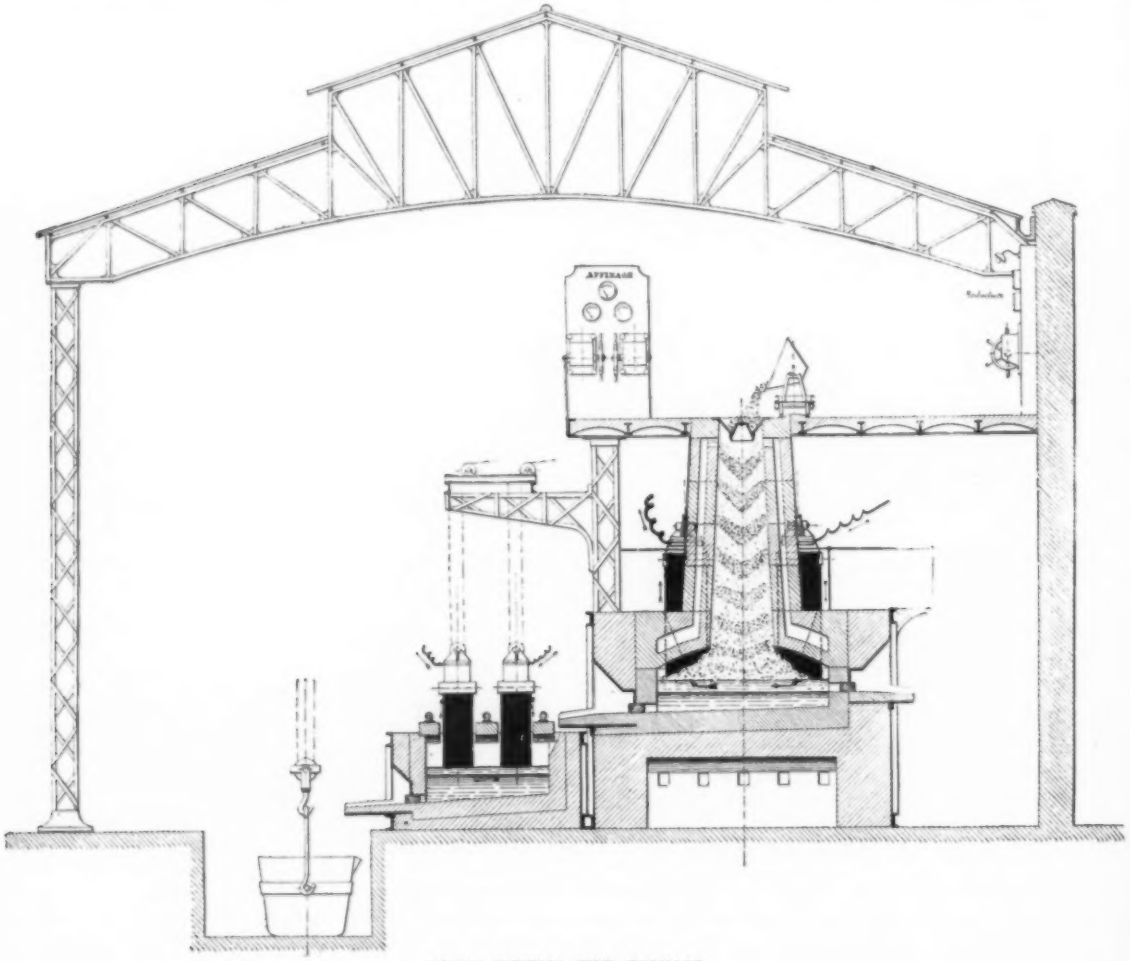
One ton of iron ore, containing 55 per cent. of iron, delivered at the plant	$2.
One ton of coke for reduction, delivered	8.
One ton of flux, delivered	3.
Price of labor per day	0.60
100 kilograms of electrodes, delivered	6.
Electrical energy, per kilowatt year of 8,400 hours	10.

This last price includes depreciation of the buildings and of the machinery. In the case of a plant of average size, the cost of manufacture of a ton of steel includes: 1. Raw materials (ore, coke, electrodes, fluxes, and special materials). 2. Electrical energy. 3. Labor. 4. Maintenance (maintenance in general, ingot moulds, refactory materials, tools). 5. General current expenses. 6. Deterioration; and the total cost* may be assumed to be about $18.

One may therefore conclude that the ton of steel made by the electric treatment direct of the ore and cast into ingots, not including the license of manufacture, can be made at a cost of $18 to $20, in round figures. For exceptionally low prices in raw materials and electrical energy the cost of manufacture could be, of course, diminished."

In the manufacture of steel from scrap iron, the output of a furnace is greater for the same power, than in the manufacture of steel direct from the ore; hence the electrical energy enters into the cost of one ton of steel as a less important item in the first case than in the second. On the other hand, in the cost of manufacture of one ton of steel, the scrap iron represents generally a larger item than the ore and the coke together. Whether the one method is superior to the other, depends therefore only on the geographical situation of the plant.

Concerning the quality of the steel produced in the Keller furnace, Mr. Bertolus reproduces extracts from a report on tests made with an ingot of this steel by the metallurgists of the Basin de la Loire. He concludes that the quality of the ordinary steel made in the electric furnace is fully satisfactory to metallurgists; the electric steel can enter into competition with the Martin (open hearth) and Bessemer steel. As in



KELLER ELECTRIC STEEL FURNACE.

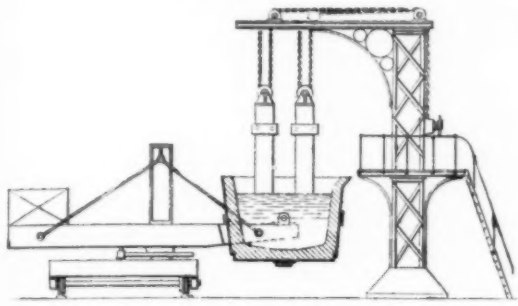
the electric furnace the heat produced is not due to an oxidizing agent, the steel which is made electrically is less liable to contain oxides of iron in solution and it can easily reach the quality of crucible steels. Moreover in comparison with the crucible process, the manufacture of steel in the electric furnace has the great advantage that it can be undertaken on a much larger scale and "it is absolutely certain that very soon the small crucibles containing 30 kilograms of steel which are at present used in the large metallurgical plants, will be replaced by large electrically-operated crucibles containing several thousands of kilograms of metal."

This is essentially the contents of Mr. C. Bertolus' interesting paper. We are indebted to Mr. P. McN. Bennie for the following additional information on improved apparatus

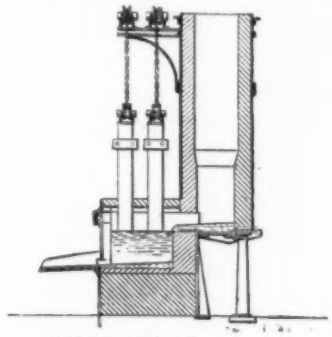
* Presumably per metric ton, *i. e.*, 1000 kg. or about 2200 pounds.

recently designed by Mr. Keller and shown in two adjoining diagrams. The one shows an arrangement in which the refining furnace is mounted upon a truck running on rails, so that it may be moved along a series of electric furnaces; the one refining furnace thus serves the whole series and is therefore almost in constant use, the economy of the process being thereby increased. The other diagram shows an arrangement in which the refining furnace is operated in conjunction with the ordinary foundry cupola.

Mr. P. McN. Bennie points out that the problem should



LADLE FURNACE.



CASCADE FURNACE.

be of great interest to American metallurgists in view of the great water-power developments in the neighborhood of the Lake Superior ore deposits, and of the titaniferous iron ores in New York State and Canada. On the other hand, he calls attention to the fact that the application of electric-furnace methods is not restricted to regions with water power. The blast-furnace gases may be utilized for driving gas engines coupled with electric generators, so that the electric-furnace process might be worked in conjunction with blast furnaces.

SOME LABORATORY OBSERVATIONS ON ALUMINIUM.

By Prof. C. F. Burgess and Carl Hambuechen.

WHILE Nature has rewarded modern ingenuity and enterprise in giving to mankind one of her most important treasures, she has withheld much of the knowledge relative to this important metal which is necessary in order that it may be utilized to greatest advantage.

Aluminium having become a material of every-day use, our familiarity with it is conducive to the idea of intimate acquaintance. That we are not thoroughly acquainted with it, however, is shown by the very contradictory and misleading statements made in all sincerity, even by leading authorities, relative to the properties of this metal. But it cannot appear strange that our knowledge of this metal is deficient when a thorough study reveals the fact that we really know little about the oldest and most important structural metal—iron.

Each addition to our knowledge of the properties of aluminium points the way for new applications of the metal, and the extent of its use in the future can be judged best by estimating the increase of knowledge regarding its properties. The adaptability of aluminium for a new and previously untried use can be estimated best if not alone by actual trial. Experience is, particularly in this case, the best teacher, for what reliance could be placed upon advice such as that of which the following statements quoted from authorities of note give a common illustration? "Aluminium is unaffected by either sulphuric or nitric acids," and "Sulphuric and nitric acids act immediately upon aluminium."

There are certain properties of this metal which, while known by some for a long time, have not become matters of general information. It is the purpose to point out in this paper a few such features, and to give data and results of observations made in the laboratory of applied electrochemistry of the University of Wisconsin during the past two years. Some of these observations are both contradictory and confirmatory of previously-published statements, and certain other observations, it is believed, are pointed out here for the first time.

The properties which are especially peculiar to aluminium are, in some cases, obstacles which have to be encountered and overcome in adapting the metal to certain uses, and in other cases these same properties are the ones which enable the metal to be employed for purposes that no other metal can fulfill.

Aluminium has not been used for a sufficient length of time to enable certain properties, such as corrodibility under various atmospheric conditions, to be determined. It is called by some a very corrodible metal, and by others a very durable substance, depending perhaps upon the point of view, whether theoretical or practical. Theory might indicate that aluminium occupying an electropositive position in the electrochemical series of elements may be expected to become oxidized or acted upon by an oxidizing agency with much greater readiness than all the other common metals, and this is borne out in the Goldschmidt reducing process, where aluminium, in a finely-divided form, is used as a strong reducing agent. Further, if an aluminium plate be thoroughly amalgamated and exposed to the air, it will oxidize so readily as to form in a few minutes a thick, white, voluminous layer of aluminium oxide, and the plate will become so hot as to be uncomfortable to the hand. There are no other common metals which will "burn up" so readily when placed in contact with the air.

We have, on the other hand, however, the fact that this metal may be placed in contact with either dilute or concentrated nitric acid and the corrosive action will be extremely slow, and with sulphuric acid it will also be so slow as to escape detection unless observed for a considerable length of time. Inasmuch as aluminium will resist the oxidizing action of these strongest oxidizing agents in a degree which none of the other metals, with the exception of gold and platinium, can equal, there has been some ground for the statements that aluminium behaves as a noble metal, and can be used for the cathode of a primary battery.

Many of such contradictory conclusions regarding aluminium may be based upon such factors as the use of impure aluminium in one case and aluminium of a high degree of purity in another, differences of temperature and various other considerations, including perhaps the most important of all, the well-known supposition that aluminium is covered with a thin, invisible protective film, which, under certain conditions, effectually prevents contact of the metal itself with the air, solution or other surrounding influences wherever such surrounding influences are not such as to destroy this coating. This film is supposed to have considerable strength and continuity, and if it is broken or removed by mechanical means the aluminium immediately forms a new one. If, therefore, this metal could be used as a structural material for bridges,

the maintenance of such structures would not involve an annual expenditure for painting, since they would "paint themselves."

There has been some difference of opinion as to whether such protective coating really exists, and, if so, whether it is that which influences or determines the apparent properties of the metal. It is true that the coating must be very thin; it can barely, if at all, be detected by the microscope, and it is impossible to collect enough of it for determination of composition by chemical analysis. It is variously held to be a continuous coating of aluminium oxide, or a basic compound, or a hydroxide, etc. The chemical composition has never been determined with any degree of assurance. Suffice it to say that experimental evidence seems to prove that such film exists, and some of the facts bearing on this point will be referred to in the following.

Among the problems which have received much attention, and the satisfactory solution of which has an important bearing upon the extent of the utilization of the metal, are the soldering, the electrodeposition of various metals upon aluminium and the electrodeposition of aluminium upon other conducting surfaces.

Aluminium alloys readily and through a wide range of proportions with other metals, a fact which might naturally point to the conclusion that the soldering of aluminium should be an easy matter, as should also the deposition of other metals upon its surface. Practice has shown, however, that success can be attained only by most careful operation. The principal difficulty in soldering aluminium seems to be due to the failure of the alloy used as a solder to adhere to the aluminium, a condition attributable to the protective film, which must be eliminated before the metals can unite. A great many suggestions have been made and processes patented for doing this work, although only a few have proved practical. The various methods may be classified in the divisions: those using a flux; those employing a special solder which works its way over the surface without a flux, and those depending upon the mechanical abrasion or cleaning of the surface while the solder is being applied. Combinations of the above may also be used.

The higher the temperature to which aluminium is heated, the greater is the ease with which the solder will unite, and by heating to the softening point and scratching the surface almost any solder which will melt at that temperature will flow over the aluminium surface. Possibility of damage to the aluminium article, together with the inconvenience of working at this high temperature, makes such process impracticable for most purposes, and it is really a welding rather than a soldering process.

It has been found that certain solders, properly proportioned and compounded, can be applied to aluminium quite readily without the use of a flux, and at a temperature such that the ordinary soldering copper can be used. The "tinning" of the surface is facilitated by mechanical abrasion while the solder is being applied. Of the various metals entering into the composition of such solders, the most important are zinc, tin, aluminium, lead, nickel, copper and bismuth. Just what functions the different ingredients fulfill is perhaps unknown. It may be that certain metals give to the solder the ability to work its way or flow by capillarity or otherwise under the surface film on the aluminium, and thus alloy with the metal. Zinc seems to possess this property to the most marked degree.

A successful solder of this sort, which is now on the market and in quite extensive use, has a composition something as follows: Zinc, 21 per cent.; tin, 76 per cent., and aluminium, 3 per cent. This may be applied directly to a cleaned aluminium surface without the use of a flux, and at a temperature but little above that which is necessary for soldering copper or iron.

There are certain advantages in the apparent complication which the use of a flux involves. A suitable solvent for the oxide film increases the rapidity of the soldering process, increases the certainty of adhesion and enables cheaper soldering mixtures to be employed. The requirement for such a flux is that it should dissolve the coating and leave a clean surface for the solder to unite with upon application of heat. While there are various aqueous solutions, such as hydrochloric acid, hydrofluoric acid and ammonium fluoride, which are solvents for the aluminium coating, none of these substances will leave a clean surface after the application of heat. The results of a large number of tests with different materials seem to point to the fact that water cannot be a component of a suitable flux. Following this idea, a flux was made up by means of which any ordinary solder, such as 50 per cent. tin and 50 per cent. lead, may be made to readily unite with an aluminium surface which had not been previously cleaned. Such material contained potassium fluoride as the principal ingredient, potassium fluoride and resin being dissolved in acetone and a little zinc chloride added to harden the mixture. By exposure to the air, a partial solidification takes place, the resultant pasty substance being in a form suitable for a flux.

Another material which, for certain solders, forms an admirable flux is stearic acid. By applying this to a freshly-scraped aluminium surface, and then applying a tin-lead-zinc alloy, the matter of soldering aluminium presents scarcely greater difficulties than does the soldering of other metals.

This almost ever-present coating upon aluminium is the source of difficulty in the deposition of a permanent coating of other metals upon aluminium surfaces. Although aluminium itself presents a surface to atmospheric conditions which ordinarily needs no further protection by other metals and maintains a pleasing appearance, still there are many cases where it is desirable, for ornamental and protective purposes, to apply to it a durable coating of other metal. Aluminium continually coming in contact with the hands, and subjected thereby to the action of the perspiration, undergoes corrosion somewhat rapidly. A certain instance has come to the writers' attention where an aluminium handle on a certain form of tool corroded so rapidly as to become useless in a few weeks. The advantage of a protective coating of some other metal is, in this instance, evident, and many other similar cases might be cited. There is also a growing demand for gold and silver plating on aluminium objects, such as toilet articles, tableware, ornaments, etc., and a cheap and successful method of performing this operation will be of advantage to the aluminium industry.

The obstacles in this matter are, first and last, the difficulty in electrodepositing a metal which will stick. While it is a very simple matter to deposit a layer of metal upon aluminium from almost any plating solution, in the great majority of operations the resulting coating can be readily removed; sometimes in remarkably thin and continuous layers, and it is only by observing certain precautions that the resultant coating will stand the buffing or polishing operations. The writers have employed aluminium plates in the production of thin sheets of zinc, nickel and other metals, such metals, after being deposited to a desired thickness, having been separated from the aluminium by means of air pressure. Even though the coating may apparently adhere and stand the buffing operation without blistering, the success of the coating is not insured; subsequent exposure to moisture may cause the coating to become loose, or, even if no external moisture be present, the solution which may have been inclosed in the pores of the metal may spread out and cause separation of the coating.

The prime requisite in successful deposition on aluminium is the complete removal of the protective film, so that the electrodeposited metal may be applied over the complete surface of and in intimate contact with the aluminium. If this condition is fulfilled and the coating is non-porous, it will be durable.

Various formulas for carrying out this operation have been published and patented, and, while the majority of them are unsuccessful and misleading, there are certain methods of procedure through which successful results may be attained. The limits of this paper, however, do not allow a discussion of the

various processes which may be employed. As a result of laboratory investigation, it has been found that the deposition of metals upon aluminium can be carried out with the same ease, and with practically the same durability of results, at least as far as tests covering one year's time would indicate, as upon iron and other metals.

The converse of this operation, however, the electrodeposition of aluminium upon other metals, is an entirely different matter. The desirability of performing this operation has long been recognized, and has led to much experimental investigation on the deposition of aluminium from aqueous solutions, the principal object being to make the corrosion-resisting properties of aluminium available in the protection metal surfaces from corrosion, thus affording a more efficient protection than tinning or galvanizing, as now applied. Such process has not as yet shown any signs of development, although statements have been made from time to time since the discovery of aluminium that success had been attained in the deposition of aluminium from aqueous solutions, some of these statements having been contributed by men of note in the scientific world. Whether we shall conclude that such statements have been purposely misleading or made as a result of erroneous conclusion, and explain the fact that no electrolytic aluminium plating has been exhibited for public inspection because secrecy has to be maintained in regard to it, the fact is that this process has shown no outward signs of commercial success. A method of depositing aluminium from aqueous solutions would find application not only for ornamental and protective purposes, but, if such a process had been discovered, it would be heralded as a means for obtaining aluminium from its compounds.

While there do not seem to be any laws of nature which prohibit the deposition of aluminium from aqueous solutions, and while it is not beyond the range of possibility that a suitable means for doing it may be discovered, the probability is that a solution other than an aqueous one must be used. Evidence seems to point to a fact that where water is present the deposition of aluminium is prevented.

The adaptability of aluminium for electrode purposes has received some attention at the hands of electrochemists. There are certain limitations which make it unsuitable for most electrolytic operations. When used as the cathode, the tendency of the reducing action and of the gases liberated is to remove the protective film, and thus cause continual exposure of the plate to the solution and its consequent corrosion. In aluminium we have one of the few instances where the cathode is corroded, and in some cases the results are quantitative and in close agreement with the requirements of Faraday's laws.

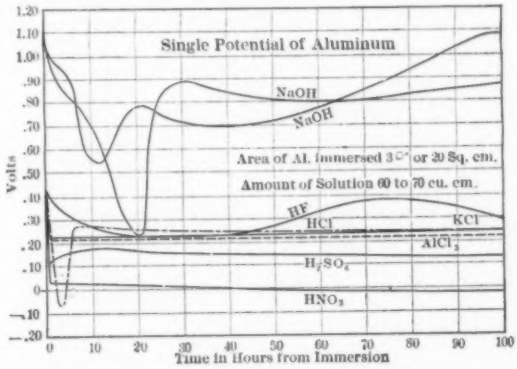
The fact that aluminium separates readily from a metal which has been electrolytically deposited upon it may be utilized to advantage in certain cases. It has been proposed to use this metal for cathodes in the electrolytic recovery of gold from cyanide solutions, the gold being easily collected as soon as a sufficient thickness has been attained, thus avoiding a smelting operation, as where lead cathodes are employed.

Aluminium as an anode frequently presents striking characteristics, due to the fact that the oxidizing action at the anode in many solutions tends to increase the durability and insulating power of the protective coating, with the result that the current may be entirely interrupted, even if a high pressure be applied. This coating has the property also of freely allowing current to flow from the electrolyte to the electrode, although not in the reverse direction, and the effectiveness with which this operates enables it to be used as an efficient check valve for the electric current, making it possible, among other uses, to obtain a unidirectional current from alternating current circuits.

If two aluminium plates be placed in a sodium-potassium tartrate solution, and an alternating pressure of about 50 volts be applied, a view of the plates in a dark room will show a distinct phosphorescence; an increase of pressure causes an exceedingly beautiful sparkling, which, on close inspection, bears a resemblance to the appearance of the heavens on a clear night, with even an imitation of the milky way; and a further increase of pressure causes a more marked sparkling effect of great brilliancy, and the possibility of adapting this phenomenon to advertising and display purposes at once suggests itself. This appears especially practical when an examination of the electrical instruments show that a very small amount of energy is necessary in producing a considerable degree of illumination, and the impression which is obtained from a bright illumination under water is sufficiently startling to be attractive.

Another way in which aluminium may play an important part in an electrochemical manner is in its use as the metal to be consumed in a primary cell for the production of electrical energy.

From the fact that, for equal weights, aluminium possesses about four times the energy as does zinc, some considerable attention has been given the matter of substituting the former metal for the zinc commonly used in primary cells or electrochemical generators of electrical energy, and various patents have been granted on means for accomplishing this. Aluminium, being a more electropositive element than zinc, might be expected to give, in combination with suitable cathode and electrolyte, a higher electromotive force than does zinc under similar circumstances. The present price of aluminium places that metal on something of a par with zinc, as far as cost of



POTENTIAL CURVES OF AN ALUMINIUM ELECTRODE.

generation of electrical energy is concerned, and the higher electromotive force and greater lightness of aluminium make it a desirable material for battery purposes when considered from the theoretical standpoint. As a matter of fact, however, aluminium does not behave well as the electropositive metal of a battery and attempts to use it in practice have almost universally failed. Its failure to give the results which might be expected can again be attributed to the partially insulating compound which forms on the aluminium surface.

The conditions under which aluminium sets up and maintains the highest values of electromotive force, together with various other factors concerning this metal, is the subject of investigation which is being carried on in our laboratory by Mr. W. R. Mott. The accompanying tables and curves derived therefrom give some of the values determined by him. These show some interesting facts concerning the behavior of aluminium in various electrolytes.

The values of single potentials here given are based upon the normal "calomel" electrode, the potential of which is assumed as — 0.56 volt. By measuring between this electrode and the aluminium in contact with the respective electrolyte, and deducting the value of the normal electrode, the value of single potential of the aluminium is determined.

The measurements were made as follows: Strips of aluminium, about 3 inches long and ½ inch wide, were cut from an aluminium sheet just as obtained from the factory. Without any preliminary cleaning or special treatment, they were immersed in their respective solutions, and a reading of potential made immediately after immersion. The strips were then

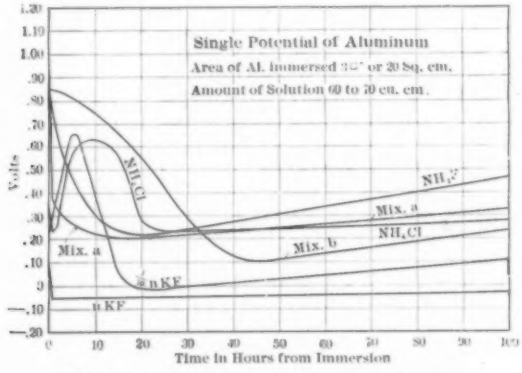
left in the solutions for about one hundred hours, and readings of potentials made at intervals during that time.

TABLE OF SINGLE POTENTIALS OF ALUMINIUM IN VARIOUS ELECTROLYTES.

Time in hours		0	.5	1.5	5.0	6.2	21.6	27.9	77.9	99.9
No.	Solution.	Volt	Volt.	Volt.	Volt.	Volt.	Volt.	Volt.	Volt.	Volt.
1.	KCl	.370	.226	.226	.226	.307	.220	.215	.232	.250
2.	$AlCl_3$	.382	.235	.220	.220	.310	.211	.220	.220	.220
3.	$AlCl_3$	.361	.211	.205	.211	.250	.199	.220	.214	.217
4.	HCl	.406	.256	-.062	.211	.271	.250	.250	.232	.232
5.	H_2SO_4	.400	.121	.139	.151	.220	.169	.160	.130	.130
6.	HNO_3	.220	.040	.040	.040	.040	-.023	.010	-.032	-.017
7.	NaOH	1.120	1.000	.964	.889	.769	.790	.721	.925	1.090
8.	NaOH	1.147	.976	.913	.826	.895	.220	.880	.820	.874
9.	HF	.430	.382	.397	.238	.250	.229	.223	.370	.289
10.	NH_4Cl	.367	.212	.274	.580	.610	.235	.232	.250	.310
11.	NH_4F	.925	.616	.595	.556	.211	.217	.370	.400	.454
12.	KF	.010	-.050	-.053	-.023	-.023	-.068	-.008	-.026	-.053
13.	KF	.223	.346	.445	.652	.610	.026	.022	.100	.040
14.	Mix. *a*	.925	.370	.319	.280	.250	.220	(*)	.274	.262
15.	Mix. *b*	.760	.850	.820	.790	.778	.529	.286	.187	.235

(*) On allowing current to flow, potential rose from .220 to .403 volt.

Solutions 1, 4, 5, 6, 7, 9, 10, 11 and 12 were normal solutions; 2 was dilute solution of aluminium chloride, commercial; 3, dilute solution of pure aluminium chloride; 8 was 0.1 normal solution of sodium hydroxide; 13, a 0.1 normal solution of potassium fluoride; 14, a mixture of equal parts of normal ammonium chloride and normal ammonium fluoride; 15 was a mixture of normal ammonium chloride and 0.1 normal potassium fluoride.



POTENTIAL CURVES OF AN ALUMINIUM ELECTRODE.

From the first column of values, it will be noted that the potential of aluminium at the moment of immersion in various electrolytes has widely different values, depending upon the solution employed. The lowest value here given is 0.01 volt in potassium fluoride, and the highest 1.147 volts in sodium hydroxide.

The data here given would point to the conclusion that, of the various materials tested, ammonium fluoride would be the best material to use in connection with aluminium for battery purposes, the use of this being analogous to the use of ammonium chloride in connection with zinc in the ordinary type of open-circuit cell. Tests which were made showed that an aluminium-consuming cell of this type would set up a pressure of almost 2 volts. The factors governing commercial operation, such as constancy of pressure on open and closed circuit, the consumption of aluminium and electrolyte, polarization, etc., have not been completely investigated.

It will be noted, from measurements taken at intervals covering a period of one hundred hours, that the general tendency is for the single potential to decrease, though there are instances when the pressure increases to some degree. The variations are shown in the curves, some of which exhibit marked irregularities, which may indicate certain properties of the metal, or they may have been accidental, the results of errors of observation or other factors. An investigation of such irregularities is the subject of further investigation.

Aluminium shows greater variations in its contact potentials with different solutions than perhaps any other metal. Chromium has been shown to exhibit three widely different values of single potential, depending upon different stages of oxidation which it may undergo, it being capable of combining in three different valencies. A similar assumption in the case of the variations in the single potentials of aluminium can hardly hold, and the explanation must be sought elsewhere. One such is that in certain cases, those in which we obtain the highest values, it is the potential of the metal itself which is being determined. In other cases it may be that the aluminium, wherever its protective coating is fractured or perforated so as to allow its coming in contact with the solution, coats itself with a layer of hydrogen, and it is really the single potential of hydrogen which we are measuring. Or, further, the aluminium coating may itself set up a single potential, being a conductor of sufficient conductivity to allow the measurement being taken, and there seems to be some evidence pointing to different kinds of coatings in different solutions.

The influence of the protective coating which normally exists on aluminium, after exposure to the air, is shown in the curve for ammonium chloride. The potential upon immersion is low, then rises for several hours, indicating a very slow dissolving action of the solution upon the coating, and then the potential gradually falls. The maximum point in the curve comes very much quicker, as shown in curve for mixture *b*, No. 15, where a small amount of potassium fluoride, a partial solvent for the coating, was present. With mixture *a*, No. 14, the solvent action of the ammonium fluoride was so great as to cause the aluminium to assume its maximum value of potential immediately upon dipping in the solution.

The data here given shows a number of notable peculiarities, one being the fact that aluminium in contact with the normal potassium fluoride solution gave a much lower value, at least for the first half of the time, than did the one-tenth normal solution of the same salt. A change of concentration, with a solution of ammonium nitrate from 0.018 normal to 4.66 normal, produced a difference of only 0.1 volt, and the change of value did not seem to be a function of the concentration.

It is possible that some of these peculiarities may be explainable on errors of observation, or they may be due to different physical condition of the aluminium samples, although care was taken to cut all the pieces tested as nearly of a size as possible from an aluminium sheet and subjecting them all to similar treatment. That the physical condition of the aluminium may exert a large influence was shown by measuring the potential of an aluminium strip as cut from the sheet and again measuring it after having been hammered between aluminium plates. Differences of potential of considerable amounts were thereby produced.

The temperature is another factor which may play an important part. A rise in temperature causes a large increase of pressure in some cases and a much smaller one in others, and it may even cause a decrease in the value of the single potential.

Cleveland as a Center in Electrochemical Development.—We have received a small pamphlet containing a reprint of a recent article by Mr. Cecil L. Saunders in *Electrical World and Engineer.*

The article is a review chiefly of the work done with the electric furnace by the Cowles brothers, although later developments are also mentioned. In a general way, the application of the electric furnace to various metallurgical processes is sketched.

Some historical and personal notes are added. From the data given, it is interesting to note how many of our most successful electrochemical engineers were formerly in some way connected with Cleveland. No detailed technical information is given in the pamphlet on the processes which are mentioned.

TABLE OF ELECTROCHEMICAL EQUIVALENTS AND THEIR DERIVATIVES.

BY CARL HERING.

In view of the more accurate determinations of the atomic weights and of the electrochemical equivalent of silver which have recently been made, and are now adopted almost universally, the electrochemical equivalents of all the elements which are likely to occur in practice or in experimental research have been recalculated on the above bases under the direction of the writer, and the results are given in the accompanying table, together with many of their derivatives. The table contains not only the data generally given in other tables, but many other elements and valencies in addition, besides a number of new columns which will often be found very useful.

The atomic weights used as a basis are those given in the eighth annual report of the Committee on Atomic Weights of the American Chemical Society, published by the well-known authority F. W. Clarke in the journal of that Society for February, 1901. The values are those generally adopted by chemists in this country. They differ but very slightly from the standard values adopted in Germany, many being, in fact, identical. The atomic weights given in this table are for oxygen = 16, and not for hydrogen = 1, as the former are more generally used; but the electrochemical equivalents and their derivatives are, of course, independent of these arbitrary bases, and are therefore exactly the same for both. The only alteration made by the present writer in these values of the atomic weights was to change that of silver from 107.92 to 107.93. The latter conforms with the German table and that of T. W. Richards, and is probably the more accurate; but the chief reason for making this very slight change is that the value 107.93, when taken together with the international standard value of the electrochemical equivalent of silver, 0.001118 grams, gives 96,538.5 coulombs for the ionic charge per uni-valent gram ion, and this is in practical agreement with the abbreviated value 96,540, which is so commonly used in all countries. The adoption of 107.93, instead of 107.92, for the atomic weight of silver therefore makes the agreement between some of the different units used by electrochemists almost absolute, and is therefore thought to be justified. As the difference between 107.93 and 107.92 is only 1-100 of 1 per cent., it is, moreover, absolutely negligible in almost all cases.

The other fundamental value used in this table is the electrochemical equivalent of silver, namely, 0.001118 gram per coulomb, which was adopted by the International Electrical Congress, at Chicago, in 1893.

The value of the ionic charge which necessarily results from these two fundamental values is 96,538.5 coulombs per univalent gram ion, which is in practical agreement with the abbreviated value 96,540 in common use, the difference involving only unwarranted accuracy.

The column containing the valencies has also been headed "change of valency." The reasons for this will be explained below. It will suffice to say here that the latter term is the rational and more accurate way of stating that which concerns the electrochemist, and it simplifies many of the calculations. Every quantitative calculation of electrolytic action involves a change of valency, or a difference between two valencies, while only certain ones (though perhaps the majority in ordinary practice) involve directly the whole of the valency itself. It is for this reason that this column contains some numbers which may never occur as valencies, but which do occur as changes of valency. For the ordinary and more usual case of the setting free of an element (such as a metal or gas) at the electrodes, the change of valency and the valency itself are the same thing, as the valency of a free element is zero, and in such cases either term is correct. In many cases the equivalents for a change of valency equal to unity have been added, so that those for any other changes of valency may then be easily calculated by mere multiplication or division by a single digit. The formulas at the end of the table give the reduction factors for calculating the electrochemical equivalents and their derivatives for any other atomic weight or changes in valency than those given in the table. For instance, if n is the equivalent given in any one of these columns for a valency a, then for a different valency b this number n must be multiplied by either $(a \div b)$ or by $(b \div a)$, as indicated. This is always a very simple calculation, as the valencies are always simple digits. The last line gives the factors with which any of these electrochemical equivalents can be calculated for any element, the atomic weight (for $O = 16$) being represented by y and the valency by x.

The last eight columns also give the energy equivalent per volt, from which the energy may be determined directly for any other voltage by merely multiplying or dividing by that voltage. These numbers, of course, can be used equally well with the theoretical as with the actual voltage to calculate the theoretical or the actual energy respectively. The value for the horse-power which was used in the last four columns is 745.650 watts, which is the latest and best value obtainable.

In all cases the reciprocal values are also given, so that every calculation can be made by a multiplication as distinguished from a long division. Many of the values are given to a greater accuracy than would be justified by the original data, as the first two or three left-hand figures suffice for most calculations. The object of this accuracy is to enable new values to be determined by mere proportion for any more accurate or different values of the atomic weights that may be found in the future or may be preferred. The electrochemical equivalents and their derivatives, as given in the table, are exactly correct for the values of the atomic weights there given, excepting, of course, the usual slight inaccuracy of the last right-hand digit. The calculations have been made very carefully to five and six places of figures, and were subsequently checked. It is therefore believed there are no errors. Should, however, any errors be discovered, the writer will be greatly obliged if the correction be sent to this journal, as it is the intention to make this table a standard one.

APPLICATION OF THE TABLE.

A correct knowledge of what the valencies are is of the utmost importance. The amount of copper deposited per ampère hour from a cuprous solution, for instance, is just twice as great as that from a cupric solution, because the valency is half as great in the former and the amount per ampère hour is inversely proportional to the valency. How to find what the valency is will be described later.

The following examples will serve to illustrate the application of the table; they also serve as typical methods of solving more or less difficult problems involving Faraday's law:

Simplest Case: Deposition or Solution.—The valency of any element in its free, uncombined state is assumed to be always zero, hence when an element is set free electrolytically the change of valency which it has undergone is always equal to the whole valency. These are the simplest cases to calculate, and include the majority occurring in ordinary practice, as what one generally desires to know is how much metal, gas, etc., will be set free from its solution or dissolved per ampère hour. In such cases all that is necessary is to find out what the valency of that element is in the electrolyte, then look for it in column 2 of the table, and the desired electrochemical equivalent or derivatives from it will then be found to the right in one of the different columns.

Example.—How many grams of silver will be deposited in a silver voltameter by 5 ampère hours? The electrolyte is always nitrate of silver, $AgNO_3$, in which the valency of the silver is I. In the table after Ag and valency I, the figure under grams per ampère hour is 4.02, which, multiplied by 5, gives 20.10 grams.

How many pounds of zinc will be consumed (not including local action, of course) in the usual chromic acid battery for 10 available horse-power hours if the available voltage is 1.7?

TABLE OF ELECTROCHEMICAL EQUIVALENTS

AND THEIR DERIVATIVES.

Symbol.	Valency, or change of valency.	Atomic weight; Oxygen = 16 (Clarke).	Milligram per coulomb.	Coulomb per milligram.	Grams per ampère hour, or Gr. per watt-hr. when ÷ by volts, or Klgr. per k.w.-hr. when ÷ by volts.	Ampère-hours per gram, or Watt-hrs. per gr. when × by volts, or K.w.-hrs. per klgr. when × by volts.	Pounds per 1,000 ampère hours, or Pounds per k.w-hr. when ÷ by volts.	Ampère-hours per pound, or Watt-hours per pound when × by volts.	Kilograms per horse-power-hour when ÷ by volts.	Horse-power-hours per kilogram when × by volts.	Pounds per horse-power-hours when ÷ by volts.	Horse-power-hours per pound when × by volts.
1	2	3	4	5	6	7	8	9	10	11	12	13
Ag	1	107.93	1.1180	0.8945	4.0248	0.24846	2.873	112.70	3.0011	0.33321	6.616	0.15114
Al	3	27.1	0.09357	10.687	0.33686	2.9686	0.7427	1346.5	0.25118	3.9812	0.5538	1.8058
As	1	75	0.7769	1.2872	2.7968	0.35753	6.166	162.18	2.0855	0.47951	4.5975	0.21750
"	3		0.25896	3.8615	0.9323	1.0726	2.0553	486.55	0.6952	1.4385	1.5325	0.6525
Au	1	197.2	2.0427	0.48954	7.354	0.13599	16.212	61.68	5.483	0.18237	12.089	0.08272
"	3		0.6809	1.4686	2.4513	0.40796	5.404	185.05	1.8278	0.5471	4.0296	0.24817
B	3	11.0	0.037981	26.329	0.13673	7.314	0.30144	3317.4	0.10196	9.808	0.22477	4.4490
Ba	2	137.40	0.7116	1.4052	2.5619	0.3903	5.648	177.05	1.9103	0.5235	4.2114	0.23745
Bi	1	208.1	2.1556	0.46390	7.760	0.12886	17.108	58.45	5.786	0.17282	12.756	0.07839
"	3		0.7185	1.3917	2.5867	0.38659	5.703	175.35	1.9288	0.5185	4.2523	0.23517
Br	1	79.95	0.8282	1.2075	2.9814	0.33541	6.573	152.14	2.2231	0.44983	4.9011	0.20404
C	1	12.0	0.12430	8.045	0.44749	2.2347	0.9866	1013.6	0.33367	2.9969	0.7356	1.3594
"	4		0.031076	32.179	0.11187	8.939	0.24664	4054.5	0.08342	11.988	0.18390	5.438
Ca	2	40.1	0.20769	4.8149	0.7477	1.3375	1.6484	606.7	0.5575	1.7937	1.2291	0.8136
Cd	2	112.4	0.5822	1.7178	2.0957	0.47716	4.6203	216.43	1.5627	0.6399	3.4451	0.29026
Cl	1	35.45	0.36721	2.7232	1.3220	0.7565	2.9144	343.12	0.9857	1.0145	2.1731	0.46016
Co	1	59.00	0.6112	1.6363	2.2002	0.45451	4.8506	206.16	1.6405	0.6096	3.6168	0.27649
"	2		0.30558	3.2725	1.1001	0.9090	2.4253	412.33	0.8203	1.2191	1.8084	0.5530
"	3		0.20372	4.9087	0.7334	1.3635	1.6168	618.5	0.5469	1.8287	1.2056	0.8295
Cr	1	52.1	0.5397	1.8530	1.9429	0.5147	4.2832	233.46	1.4487	0.6903	3.1938	0.31311
"	2		0.26984	3.7059	0.9714	1.0294	2.1416	466.93	0.7243	1.3806	1.5969	0.6262
"	3		0.17989	5.559	0.6476	1.5441	1.4278	700.4	0.48290	2.0708	1.0646	0.9393
Cu	1	63.6	0.6588	1.5179	2.3717	0.42164	5.229	191.25	1.7685	0.5654	3.8988	0.25649
"	2		0.32940	3.0358	1.1858	0.8433	2.6143	382.50	0.8842	1.1309	1.9494	0.5130
F	1	19.05	0.19733	5.068	0.7104	1.4077	1.5661	638.5	0.5297	1.8879	1.1678	0.8563
Fe	1	55.9	0.5790	1.7270	2.0846	0.47972	4.5956	217.59	1.5544	0.6434	3.4268	0.29182
"	2		0.28952	3.4540	1.0423	0.9594	2.2978	435.19	0.77718	1.2867	1.7134	0.5836
"	3		0.19301	5.181	0.6949	1.4392	1.5319	652.8	0.5181	1.9301	1.1423	0.8755
Gl	2	9.1	0.047131	21.217	0.16967	5.894	0.37407	2673.3	0.12652	7.904	0.27892	3.5852
H	1	1.008	0.010441	95.77	0.037589	26.603	0.08287	12067.	0.028028	35.678	0.06179	16.183
Hg	1	200.0	2.0717	0.48269	7.458	0.13408	16.442	60.82	5.561	0.17982	12.260	0.08157
"	2		1.0359	0.9654	3.7291	0.26817	8.221	121.64	2.7806	0.35964	6.130	0.16313
I	1	126.85	1.3140	0.6478	4.7303	0.21140	10.429	95.89	3.5272	0.28351	7.776	0.12860
Ir	1	193.1	2.0002	0.4999	7.201	0.13887	15.875	62.99	5.369	0.18624	11.837	0.08448
"	3		0.6668	1.4998	2.4003	0.41662	5.292	188.97	1.7898	0.5587	3.9458	0.25344
K	1	39.11	0.40512	2.4684	1.4584	0.6857	3.2153	311.01	1.0875	0.9196	2.3975	0.41710
Li	1	7.03	0.07282	13.732	0.26215	3.8145	0.5780	1730.2	0.19548	5.116	0.43095	2.3205
Mg	2	24.3	0.12586	7.946	0.45308	2.2071	0.9989	1001.1	0.3378	2.9600	0.7448	1.3426
Mn	1	55.0	0.5697	1.7553	2.0510	0.48757	4.5216	221.16	1.5293	0.6539	3.3716	0.29660
"	2		0.28486	3.5105	1.0255	0.9751	2.2608	442.31	0.7647	1.3078	1.6858	0.5932
"	3		0.18991	5.266	0.6837	1.4627	1.5072	663.5	0.5098	1.9617	1.1239	0.8898
Mo	2	96.0	0.49721	2.0112	1.7900	0.5587	3.9462	253.41	1.3347	0.7492	2.9425	0.33985
N	1	14.04	0.14543	6.876	0.5236	1.9100	1.1543	866.4	0.39039	2.5615	0.8607	1.1619
"	3		0.048478	20.628	0.17452	5.730	0.38475	2599.1	0.13013	7.685	0.28689	3.4856
Na	1	23.05	0.23876	4.1882	0.8596	1.1634	1.8950	527.7	0.6409	1.5602	1.4130	0.7077

1	2	3	4	5	6	7	8	9	10	11	12	13
Ni	I	58.70	0.6080	1.6446	2.1890	0.45684	4.8258	207.22	1.6322	0.6127	3.5984	0.27790
"	2		0.30402	3.2892	1.0945	0.9137	2.4129	414.43	0.8161	1.2253	1.7992	0.5558
"	3		0.20268	4.9338	0.7297	1.3705	1.6086	621.7	0.5441	1.8380	1.1995	0.8337
O	I	16.000	0.16574	6.034	0.5967	1.6760	1.3154	760.2	0.44489	2.2477	0.9808	1.0196
"	2		0.08287	12.067	0.29833	3.3520	0.6577	1520.5	0.22245	4.4954	0.49041	2.0391
Os	2	191.0	0.9892	1.0109	3.5613	0.28080	7.851	127.37	2.6555	0.37658	5.854	0.17081
P	I	31.0	0.32112	3.1141	1.1560	0.8650	2.5486	392.37	0.8620	1.1601	1.9003	0.5262
"	3		0.10704	9.342	0.38534	2.5951	0.8495	1177.1	0.28733	3.4803	0.6335	1.5787
Pb	I	206.92	2.1434	0.46655	7.716	0.12960	17.011	58.79	5.754	0.17380	12.685	0.07884
"	2		1.0717	0.9331	3.8581	0.25919	8.506	117.57	2.8768	0.34761	6.342	0.15767
Pd	2	107.0	0.5542	1.8045	1.9951	0.5012	4.3984	227.36	1.4876	0.6722	3.2796	0.30491
Pt	4	194.9	0.5047	1.9813	1.8170	0.5504	4.0058	249.64	1.3548	0.7381	2.9869	0.33479
Rh	2	103.0	0.5335	1.8745	1.9205	0.5207	4.2339	236.19	1.4320	0.6983	3.1570	0.31675
S	I	32.07	0.33220	3.0102	1.1959	0.8362	2.6366	379.28	0.8917	1.1214	1.9659	0.5087
"	2		0.16610	6.021	0.5980	1.6724	1.3183	758.6	0.44587	2.2428	0.9830	1.0173
Sb	I	120.4	1.2472	0.8018	4.4898	0.22273	9.898	101.03	3.3477	0.29870	7.381	0.13549
"	3		0.41572	2.4054	1.4966	0.6682	3.2994	303.08	1.1159	0.8961	2.4602	0.40647
Se	2	79.2	0.41020	2.4378	1.4767	0.6772	3.2556	307.16	1.1011	0.9082	2.4275	0.41194
Si	4	28.4	0.07355	13.597	0.26476	3.7769	0.5837	1713.2	0.19742	5.065	0.43524	2.2976
Sn	2	119.0	0.6163	1.6225	2.2188	0.45069	4.8916	204.43	1.6545	0.6044	3.6474	0.27417
"	4		0.30817	3.2450	1.1094	0.9014	2.4458	408.86	0.8272	1.2089	1.8237	0.5483
Sr	2	87.60	0.45371	2.2041	1.6333	0.6122	3.6009	277.71	1.2179	0.8211	2.6850	0.37244
Te	2	127.5	0.6604	1.5143	2.3773	0.42065	5.241	190.80	1.7726	0.5641	3.9080	0.25589
Ti	4	48.15	0.12469	8.020	0.44889	2.2277	0.9896	1010.5	0.33471	2.9876	0.7379	1.3552
U	4	239.6	0.6205	1.6117	2.2337	0.44768	4.9245	203.07	1.6656	0.6004	3.6720	0.27233
V	I	51.4	0.5324	1.8782	1.9167	0.5217	4.2258	236.64	1.4292	0.6997	3.1508	0.31737
"	2		0.26622	3.7564	0.9584	1.0434	2.1129	473.29	0.7146	1.3994	1.5754	0.6347
W	2	184.	0.9530	1.0493	3.4308	0.29148	7.564	132.21	2.5581	0.39091	5.640	0.17731
Zn	2	65.4	0.33873	2.9522	1.2194	0.8201	2.6883	371.98	0.9093	1.0998	2.0046	0.49886
Zr	4	90.4	0.23410	4.2716	0.8428	1.1866	1.8580	538.2	0.6284	1.5913	1.3854	0.7218
	a		n	n	n	n	n	n	n	n	n	n
	b		$\frac{a}{b}$ n	$\frac{b}{a}$ n	$\frac{a}{b}$ n	$\frac{b}{a}$ n	$\frac{a}{b}$ n	$\frac{b}{a}$ n	$\frac{a}{b}$ n	$\frac{b}{a}$ n	$\frac{a}{b}$ n	$\frac{b}{a}$ n
	x	y	$\frac{y}{0.010359-\frac{x}{x}}$	$\frac{x}{96.54-\frac{y}{y}}$	$\frac{y}{0.037291-\frac{x}{x}}$	$\frac{x}{26.816-\frac{y}{y}}$	$\frac{y}{0.08221-\frac{x}{x}}$	$\frac{x}{12164.-\frac{y}{y}}$	$\frac{y}{0.027806-\frac{x}{x}}$	$\frac{x}{35.964-\frac{y}{y}}$	$\frac{y}{0.06130-\frac{x}{x}}$	$\frac{x}{16.313-\frac{y}{y}}$

COPYRIGHT, 1903, BY CARL HERING

(For the atomic weights of the other elements and the full names, see table of valencies below.)

The zinc is dissolved as sulphate, and always has a valency of II. From the table under Zn II, the pounds per horse-power hour for 1 volt (column 12) is 2.00, which, divided by 1.7 volts, gives 1.18 pounds per horse-power hour, and this, multiplied by 10, gives 11.8 pounds. For the theoretical amount of energy, use the theoretical instead of the available voltage.

In the same way the amount of any element set free or dissolved by a given current or amount of energy, or the current or energy required for or given out by the setting free or dissolving of a given amount of any element, may be readily calculated directly from the figures in the table. When calculations involving the energy are made for both of the two electrodes, it must not be forgotten that the voltage measured at the terminals of the cell applies to the sum of both reactions taken together, and not to each one separately. This same voltage is used to calculate the total energy, irrespective of whether the calculation is based on the reaction at the anode or the cathode, and the energies must therefore not be added together when both are involved, as the same energy performs both operations. When the local energy at each electrode is calculated separately, as, for instance, from the thermochemical data, the two energies must, of course, be added to give the total: care must then be taken to add them algebraically, as they may have different signs. In the Daniell cell, for instance, energy is given out at the zinc electrode, but is absorbed at the copper, and the total is therefore the difference.

Simple Case of Change of Valency.—In many cases the element is neither set free nor dissolved; it simply changes its valency from one value to another. Such, for instance, is the case in the action of many of the so-called depolarizers, like the peroxide of manganese of the Leclanche cell, the peroxide of lead in the lead accumulator, the chromic acid or nitric acid in the Grove or the Bunsen cells. In such cases, find the valencies before and after the reaction, and the difference will give the change of valency which is to be used in obtaining the equivalents from the table. (The sign of this difference indicates the direction of the current, and is therefore not involved in the numerical values.)

Example.—How much manganese is involved in a discharge of 100 ampère hours from a Leclanche cell? In this case $2MnO_2$ changes into Mn_2O_3. The valency in the first is IV and in the second III, hence the change is I. The table gives 2.05 grams per ampère hour for Mn, with a change of valency of I, hence for 100 ampère hours the amount of the element manganese involved is 205 grams. The amount of the peroxide corresponding to this is then found, as usual, by the well-known chemical calculation; thus the molecular weight of the peroxide MnO_2 is $55 + (2 \times 16) = 87$, and that of the manganese is 55; hence $205 \times (87 \div 55) = 324$ grams MnO_2.

Those who do not wish to use this simple method, based on changes of valencies, may obtain the same result by the more lengthy and indirect chemical calculation. In such a case

write out the complete chemical equation, involving the zinc, the manganese and the ammonium chloride. Then calculate electrochemically the amount of zinc involved, as described above, and from this determine by purely chemical calculations the amount of the manganese or peroxide which corresponds to that amount of zinc. This will be illustrated in another example.

Example Illustrating that the Subscripts May be Ignored.—How much oxygen will be set free per ampère hour in electrolyzing sulphuric acid, H_2SO_4? The change of valency of oxygen is its full valency II, as it is set free; the result is therefore taken directly from the table, namely, 0.30 gram. It will be seen that this does not involve the subscript 4. It will be the same for H_2O where the subscript is 1. The amount set free per ampère hour is a fixed and definite quantity, and is entirely independent of any arbitrary chemical formulas, provided only that the valency be known; and in the case of oxygen it is always II.

Similarly, in the case of cuprous chloride, CuCl, the amount of chlorine set free per ampère hour is the same as in cupric chloride, $CuCl_2$, namely, 1.32 gram per ampère hour, although the subscript is twice as great in the latter case. But the amount of copper deposited per ampère hour is twice as great from the former than from the latter, because the valency is half as great.

Example Illustrating that Coefficients and Intermediate Reactions Can Be Ignored.—How much nitric acid will be required in a Bunsen cell for 100 ampère hours, assuming that the nitric acid (HNO_3) is all reduced to nitric oxide (NO)? The chemical equation of the complete reaction is

$$3Zn + 3H_2SO_4 + 2HNO_3 = 3ZnSO_4 + 2NO + 4H_2O.$$

It will be noticed that to satisfy this equation there must be three molecules of zinc and only two of nitric acid, and it is very important to include those coefficients in making the purely chemical calculation. In the direct electrochemical calculation, however, these coefficients may be ignored entirely, and, in fact, need not be known at all, as the amount of any element corresponding to an ampère hour is a fixed and definite quantity as given in the table, and is independent of any equations or coefficients like these, the only factor that needs to be known being the change of valency.

Furthermore, in the reaction the zinc is dissolved in sulphuric acid, and the corresponding hydrogen reduces the nitric acid. It thus involves the intermediate reaction of the sulphuric acid. But in the direct electrochemical calculation of the nitric acid this intermediate reaction may also be completely ignored, as the amount of nitric acid reduced per ampère hour is, as said above, a fixed and definite quantity, which is entirely independent of any intermediate reactions, provided only that the change of valency is known.

The amount of nitric acid can therefore be calculated independently of either the coefficients or the consideration of any intermediate reactions that may be involved in the complete chemical equation. It is necessary only to know what it is changed into, so as to be able to find the change of valency. In the nitric acid the valency of the nitrogen is V, and in the nitric oxide it is II; hence the change in III, and, from the table, the amount of nitrogen for this change of valency is 0.1745 grams per ampère hour—that is, 17.45 grams for the 100 ampère hours. From this the amount of the acid is then readily calculated by the usual chemical method, as follows: The atomic weight of N is 14, and of nitric acid $1 + 14 + (16 \times 3) = 63$, therefore $17.5 \times (63 \div 14) = 78.5$ grams of nitric acid.

As stated in the previous examples, this same result may also be determined indirectly by starting with the amount of zinc corresponding to the 100 ampère hours, and then, by means of the above chemical equation, calculating the corresponding amount of nitric acid by plain chemical calculations. The change of valency of the nitrogen need not then be known, but the coefficients and the intermediate reactions must be known. The amount of zinc per ampère hour, from the table, is 1.22 grams (the valency of zinc being always II), or 122 grams for 100 ampère hours. From the equation, every three atoms of zinc require two molecules of nitric acid; the atomic weight of zinc is 65.4, and the molecular weight of nitric acid is 63. Hence the 122 grams of zinc must be multiplied by 2×63 and divided by 3×65.4, which gives 78.4 grams of nitric acid, as before, neglecting the slight inaccuracies due to the abbreviated numbers.

Example Involving a Change of Sign of the Valency.—How much sulphur is involved per ampère hour in the oxidation of sulphuretted hydrogen, H_2S, into sulphuric acid, H_2SO_4? The equation is

$$H_2S + 4H_2O = 4H_2 + H_2SO_4.$$

In all the previous examples illustrating the more usual cases, the valencies of the element had the same sign before and after electrolysis, and their signs need therefore not be considered. In some cases, however, like in the present one, the sign of the valency changes, and therefore becomes very important. In every compound the bonds representing the valency must always add to zero. Those of hydrogen are always +, and of oxygen always —. In H_2S, therefore, the S must have two negative bonds (valency—II) to neutralize the two positive bonds of H_2; but in H_2SO_4 the S has six positive bonds (valency + VI), hence the change of valency is the *algebraic* difference, namely, 8 (the sign of which is of no importance here). The table does not contain this valency, but the result is easily obtained by dividing that for a valency of 1, namely, 1.20 by 8, as the amount per ampère hour decreases in proportion as the valency increases. This gives $1.20 \div 8 = 0.15$ gram of S per ampère hour. A change of sign of the valency from — to + implies oxidation (or perduction), and from + to —, reduction.

As in the previous example, the same result may also be obtained indirectly by starting with the amount of hydrogen liberated, and then calculating by purely chemical methods how much sulphur is involved in that equation. The change of valency or the change of sign need not then be known. From the table, 1 ampère hour sets free 0.0376 gram of hydrogen. From the last half of the above equation, every eight atoms of hydrogen set free correspond to one of sulphur in the H_2SO_4 formed. The atomic weight of sulphur is 32, hence $0.0376 \times (32 \div 8) = 0.15$ gram, the same as before.

In the reduction of nitric acid to ammonia in the presence of sulphuric acid, there is also a change of sign in the valency, but in this case from + to —, as it is a reduction. The equation is

$$2(HNO_3) + H_2SO_4 + 2H_2O = (NH_4)_2SO_4 + 4O_2.$$

In the nitric acid the valency of the N is + V, and in the ammonium sulphate is —III; hence the change of valency is 8. Or the calculation may be made indirectly by starting with the amount of oxygen set free, and then calculating by purely chemical methods the corresponding amount of nitrogen or nitric acid involved.

Example Illustrating a Partial Change of Valency.—How much nitric acid is required per ampère hour when used as a depolarizer in the Bunsen cell, assuming the nitric acid to be changed into ammonium nitrate? The complete reaction is

$$4Zn + 4H_2SO_4 + 2HNO_3 = 4ZnSO_4 + 3H_2O + NH_4NO_3.$$

The nitrogen in the nitric acid has a valency of +V, and in the NH_4 of the ammonium nitrate, —III; hence the change of valency is 8. Part of the nitrogen, however, does not change its valency, but remains as NO_3, and is therefore not involved in the electrochemical equivalent, the nitric acid thus performing a double duty. The equation shows that half of the N is involved in the change to NH_4, and the other half remains as NO_3. The former is calculated electrochemically, as above described, and the amount found must then be doubled in order to get the total.

The same result may be obtained indirectly by starting with the amount of zinc involved per ampère hour, and then calcu-

LIST OF THE ELEMENTS WITH THEIR SYMBOLS AND PRACTICAL VALENCIES.

(By the word "salts" is meant oxides, sulphides, sulphates, chlorides, chlorates, etc.)

Name	Symbol	Atomic Weight	Valencies
Aluminium	Al	27.1	Salts +III; aluminates +III.
Antimony	Sb	120.4	Antimonous salts +III; antimonic salts +V; antimonites +III; antimonates +V; antimonides —III, sometimes —I and —II.
Arsenic	As	75.0	Arsenious salts +III; arsenic salts +V; arsenites +III; arsenates +V; arsenides —III, sometimes —I and —II.
Barium	Ba	137.40	Salts +II.
Beryllium	Be	9.1	Salts +II. (Same element as glucinum.)
Bismuth	Bi	208.1	Bismuthous salts +III; bismuthic salts and bismuthates +V.
Boron	B	11.0	Salts +III; borates +III.
Bromine	Br	79.95	Bromides —I; hypo-bromites +I; bromates +V.
Cadmium	Cd	112.4	Salts +II.
Cæsium	Cs	132.9	Salts +I.
Calcium	Ca	40.1	Salts +II.
Carbon	C	12.0	Carbonates +IV; salts usually +IV; in CO +II; hydrocarbons, free valencies —I to —IV.
Cerium	Ce	139.0	Cerous salts +III; ceric salts +IV.
Chlorine	Cl	35.45	Chlorides —I; hypochlorites +I; chlorites +III; chlorates +V; perchlorates +VII; monoxide +I; dioxide or peroxide +IV.
Chromium	Cr	52.1	Chromous salts +II; chromic salts +III; trioxide +VI; chromites +III; chromates or di-chromates +VI.
Cobalt	Co	59.00	Cobaltous salts +II; cobaltic salts +III.
Columbium	Cb	93.7	CbO +II; CbO_2 +IV; columbic salts and columbates +V. (Same as niobium.)
Copper	Cu	63.6	Cuprous salts +I; cupric salts+II.
Didymium	Di		(See neodymium and praseodymium.)
Erbium	Er	166.0	Salts +III.
Fluorine	F	19.05	Fluorides —I; all compounds —I.
Gallium	Ga	70.0	Salts +III.
Germanium	Ge	72.5	Germanious salts +II; germanic salts +IV; germanites +II; germanates +IV.
Glucinum	Gl	9.1	Salts +II. (Same element as beryllium.)
Gold	Au	197.2	Aurous salts +I; auric salts +III; aurates +III.
Hydrogen	H	1.008	Always +I.
Indium	In	114.0	Salts +III.
Iodine	I	126.85	Iodides —I; hypoidites +I; iodates +V; periodates +VII; iodic oxide +V.
Iridium	Ir	193.1	Iridous salts +III; iridic salts +IV.
Iron	Fe	55.9	Ferrous salts +II; ferric salts +III; ferrates +VI.
Lanthanum	La	138.6	Salts +III.
Lead	Pb	206.92	Usual salts or plumbic salts +II; di-oxide or peroxide and plumbates +IV; sub-oxide +I.
Lithium	Li	7.03	Salts +I.
Magnesium	Mg	24.3	Salts +II.
Manganese	Mn	55.0	Manganous salts +II; manganic salts +III; di-oxide or peroxide +IV; manganates +VI; permanganates +VII.
Mercury	Hg	200.0	Mercurous salts +I; mercuric salts +II.
Molybdenum	Mo	96.0	Molybdous salts +II; molybdic salts +III; di-oxide +IV; trioxide and molybdates +VI.
Neodymium	Nd	143.6	Salts +III.
Nickel	Ni	58.70	Nickelous salts +II; nickelic salts +III.
Niobium	Cb	93.7	(See columbium.)
Nitrogen	N	14.04	Ammonia and ammonium salts (NH_4 salts) —III; most organic nitrogen compounds —III; nitrous oxide +I; nitric oxide +II; sesqui-oxide and nitrites +III; di-oxide (peroxide) +IV; nitric anhydride and nitrates +V. (In ammonium nitrite and nitrate the N in the NH_4 radical is —III and in the acid radical +III or +V.)
Osmium	Os	191.0	Osmous salts +II; osmic salts +IV; sesqui-oxide +III; trioxide and osmates +VI; per-oxide and perosmates +VIII.
Oxygen	O	16.000	Oxides, salts, etc. —II.
Palladium	Pd	107.0	Palladous salts +II; palladic salts +IV.
Phosphorus	P	31.0	Phosphorous salts and phosphites +III; phosphoric salts and phosphates +V; phosphides —III; hypophosphites +I; hypophosphates +IV.
Platinum	Pt	194.9	Platinous salts and platinites +II; platinic salts and platinates +IV.
Potassium	K	39.11	Salts +I.
Praseodymium	Pr	140.5	Salts +III.
Rhodium	Rh	103.0	Rhodous salts +II; rhodic salts +III; di-oxide +IV.
Rubidium	Rb	85.4	Salts +I.
Ruthenium	Ru	101.7	Ruthenous salts +II; ruthenic salts +III; ruthenic anhydride and ruthenates +IV; per-ruthenic anhydride +VIII.
Samarium	Sm	150.3	Salts +III.
Scandium	Sc	44.1	Salts +III.
Selenium	Se	79.2	Selenites +IV; selenates +VI; selenides —II.
Silicon	Si	28.4	Silicides —IV; salts, oxide and silicates +IV.
Silver	Ag	107.93	Salts +I.
Sodium	Na	23.05	Salts +I.
Strontium	Sr	87.60	Salts +II.
Sulphur	S	32.07	Sulphides —II; di-sulphides —I; SO_2 and sulphites +IV; SO_3 and sulphates +VI; hyposulphites (thio-sulphates) +II; S_2O_3 +III; S_2O_7 and per-sulphates +VII.
Tantalum	Ta	182.8	Salts and tantalates +V.
Tellurium	Te	127.5	Tellurides —II; di-tellurides —I; tellurous salts +II; telluric salts and tellurites +IV; TeO_3 and tellurates +VI.
Terbium	Tr	160.	Salts +III.
Thallium	Tl	204.15	Thallous salts +I; thallic salts +III.
Thorium	Th	232.6	Salts +IV.
Tin	Sn	119.0	Stannous salts and stannites +II; stannic salts and stannates +IV.
Titanium	Ti	48.15	Titanous salts and titanites +III; titanic salts and titanates +IV.
Tungsten	W	184.	WO +II; WO_2 and WCl_4 +IV; tungstic oxide and tungstates +VI.
Uranium	U	239.6	Uranous salts +IV; uranic salts and uranates +VI.
Vanadium	V	51.4	Vanadates +V; vanadous salts +III; VO +II; VO_2 +IV.
Ytterbium	Yb	173.2	Salts +III.
Yttrium	Y	89.0	Salts +III.
Zinc	Zn	65.4	Salts +II.
Zirconium	Zr	90.4	Salts and zirconates +IV.

lating the corresponding amount of nitric acid by purely chemical methods, in compliance with the above equation. In such rare and somewhat complicated cases as this one, this indirect method will no doubt be the safer one to use by those not accustomed to the conception of negative valency or changes of valency.

Example Illustrating the Exhaustion of the Electrolyte at Both Electrodes.—How many ampère hours will it take to

extract all the lead from a solution of nitrate of lead, $Pb(NO_3)_2$, containing 100 grams of lead, when electrolyzed between platinum electrodes? In this case the solution will be reduced at the cathode, where metallic lead will be deposited, while at the anode it will be oxidized, depositing the peroxide PbO_2, thus exhausting the solution of its lead at both electrodes. Nitric acid will be formed, and it is here assumed that it will not redissolve the lead by local action.

The equation is

$$2Pb(NO_3)_2 + 2H_2O = Pb + 4HNO_3 + PbO_2.$$

From this it is seen that an equal quantity of Pb goes out at each electrode simultaneously, hence 50 grams of lead will be deposited on each electrode. From the table, 1 gram will require 0.26 ampère hours, the valency of the lead on the cathode being II; hence $50 \times 0.26 = 13.0$ ampère hours will be required. At the anode, the valency of the lead has changed from II to IV, the change of valency being therefore II, which is the same as at the cathode; hence the amount of lead must be the same at both electrodes.

As in the previous examples, this calculation may be made without a knowledge of the change of valency by calculating the amount of metallic lead deposited on the cathode, and then, by a purely chemical calculation, finding the amount at the anode from the equation. In this case the equation shows at once that the amount of Pb on each electrode is the same.

Example Illustrating a Deposition on One Electrode and a Change of the Solution at the Oother.—How much cuprous chloride will be acted upon per ampère hour when electrolyzed between platinum electrodes? At the cathode copper will be deposited, while at the anode the chlorine will "oxidize" (or perduce) the cuprous chloride (CuCl) to cupric chloride ($CuCl_2$); there will therefore be no deposit or gas formed at the anode.

The equation is

$$2CuCl = Cu + CuCl_2.$$

The change of valency of the copper is I, not II, as is more usual; hence the number of grams per ampère hour is found directly from the table under a valency of I. The amount of the cuprous chloride corresponding to this is then calculated chemically, in the usual way, from the formula CuCl. This, however, will give only that reduced at the cathode. At the anode cuprous chloride is chloridized to the cupric, and, as this is, of course, not the same as was reduced at the cathode, it must be added to the other in order to give the total required for that same ampère hour. At the anode, the valency of the copper has changed from I to II, making a change of I, and the amount will therefore be the same as at the cathode; hence the total amount of CuCl will be double the amount corresponding to the copper set free, a fact which is also clearly seen from the coefficient 2 in the equation.

The calculation can also be made chemically from the equation, after having first calculated electrochemically the amount of copper set free at the cathode.

Example Illustrating the Reduction of One Solution and the Oxidation of Another.—If the cathode is in the copper sulphate and the platinum anode in ferrous sulphate, copper will be deposited on the cathode and the ferrous sulphate will be oxidized into the ferric sulphate. The formula is

$$CuSO_4 + 2FeSO_4 = Cu + Fe_2(SO_4)_3.$$

The copper has changed its valency from II to O, and the iron from II to III, from which all the quantities can be determined by the use of the table. Or from the Cu set free the other quantities can be calculated from the equation by purely chemical calculations.

Example Illustrating a Case in Which Nothing is Set Free or Dissolved at Either Electrode.—If the platinum cathode is in a solution of ferric sulphate and the platinum anode in ferrous sulphate, then at the cathode the ferric sulphate will be reduced to ferrous, and at the anode the ferrous will be oxidized (or perduced) to ferric; no gas or metal will be set free or dissolved at either electrode. Fe ions pass from the solution around the anode to that around the cathode, and SO_4 ions pass in the reverse direction. The reaction is as follows:

$Fe_2(SO_4)_3$ (at cathode) + $2FeSO_4$ (at anode) = $2FeSO_4$ (at cathode) + $Fe_2(SO_4)_3$ (at anode).

The valency of the Fe in the ferric state is III and in the ferrous II, hence there is a change of I, from which the electrochemical equivalent is found, in the table, to be 2.08 grams per ampère hour. This means that 2.08 grams of iron in the ferrous state will be oxidized at the anode to the ferric state by one ampère hour, and that 2.08 grams of iron in the ferric state will be reduced to the ferrous state at the cathode.

It is here assumed, of course, that there is always enough of the salt present around each electrode to enable this reaction to take place, otherwise some other reactions will begin, such as the deposition of iron on the cathode (change of valency II) or the evolution of oxygen at the anode. Too strong a current will also be apt to cause other simultaneous reactions. Attention is also called to the fact that the relative velocities of migration of the ions through the diaphragm may affect the relative amounts of the salts found on the two sides of the diaphragm after the passage of the currents, as Faraday's law has nothing to do with that; but the amount of iron oxidized or reduced per ampère hour is, according to Faraday's law, a fixed and definite quantity, found from the table, irrespective of which side of the diaphragm the salt will be found on after the passage of the current.

This is a case in which the method of calculation, based on the change of valency, is far simpler than the older one, based on the chemical equation, for the reason that there is nothing tangible set free or dissolved which could be used as a basis of the calculation, as there was in all the other examples. One cannot use the iron in this case as the basis, because it has two different valencies at the two electrodes, and it would give entirely wrong results to use either of these valencies. There may be various ways of calculating the result without involving the conception of the change of valency, but the simplest one of these seems to be to start with the SO_4 ions as a basis and then determine from this, by a chemical calculation, the amount of iron involved in the reaction. This SO_4 may be assumed, for the purpose of calculation, to pass from the ferric sulphate to the ferrous sulphate, thereby reducing the former and oxidizing (or perducing) the latter. This compound ion can safely be assumed as the basis of this calculation, because it always has, in sulphates, the same valency, namely, II, and the amount involved per ampère hour, therefore, is a constant in all sulphates. This constant amount may be found from any convenient sulphate, such as sulphuric acid, for instance, H_2SO_4, and it will be the same for both the ferric as the ferrous sulphate.

From the table, the amount of hydrogen per ampère hour is 0.0376 grams, and, as the atomic weight of SO_4 is 96, and that of H_2 is 2.02, the electrochemical equivalent of SO_4 is $0.0376 \times (96 \div 2.02) = 1.79$ grams per ampère hour. At the anode, one SO_4 combines with two $FeSO_4$ to form one $Fe_2(SO_4)_3$. Therefore, as 2Fe (atomic weight $2 \times 55.9 = 111.8$) corresponds to the addition of 96 of SO_4, it follows that $1.79 \times (111.8 \div 96) = 2.08$ grams of iron are involved per ampère hour at the anode, which is the same as was found above in the first and much simpler calculation based on the change of valency of the iron. A similar calculation based on what takes place at the cathode will give precisely the same result, as here, again, 2Fe correspond to one SO_4, the only difference being that it is a loss at the cathode, while at the anode it is a gain.

Similar Example, Involving, in Addition, a Chemical Reaction.—The cathode is in a solution of chromic acid with sulphuric acid; the platinum anode is in a solution of ferrous sulphate. Nothing is set free or enters at either electrode. The complete equation is

$$2H_2CrO_4 + 6H_2SO_4 + 6FeSO_4 = Cr_2(SO_4)_3 + 8H_2O + 3\,Fe_2(SO_4)_3.$$

The chromic acid will be reduced, which would form a precipitate; but this is soluble in the H_2SO_4, forming chromium sulphate. The Cr has changed its valency from VI to III, hence the change of valency is III. At the anode, the ferrous sulphate has changed to the ferric, the iron having changed its valency from II to III. The sulphuric acid has a double function; half of it is electrolyzed, the SO_4 going to make the ferric sulphate and the H_2 forming water, while the other half acts purely chemically by dissolving the reduced chromic acid, forming chromium sulphate and water. The latter half of the sulphuric acid would therefore not be included in the electrochemical equivalent, but must be added to that found from the table. In such cases it is safest to use the chromium or the iron in the electrochemical calculations, and then calculate the required amount of sulphuric acid from the above chemical equation. It may be of interest to note here that this reaction forms an odd kind of accumulator, in which only the liquids enter into the reaction, the plates themselves remaining completely unchanged.

Here, again, the more complicated method of calculation, based on the chemical equation, might be used, as was shown in the previous problem, taking one SO_4 as a basis and calculating the other quantities from it.

HOW TO DETERMINE THE VALENCY.

In order to use this simpler method of change of valency in calculations involving the electrochemical equivalent, it is very necessary, of course, to know what the valencies are. Those who cannot determine these changes in valencies with the assistance indicated below must use the older, indirect and generally more lengthy chemical calculation, after having determined electrochemically the amount of some one convenient quantity in the equation.

It would be difficult, if at all possible, to give complete rules for determining the valencies, nor is it the object to do so here. The simplest way is to get them from the table which follows, and which was kindly prepared for this article by Prof. J. W. Richards. It gives what he calls the "practical valencies;" that is, the actual valency, irrespective of any interpretation involving a structural formula. He also gives their signs. There are others which occur more rarely, and still others about which there is some doubt. In such cases the safest method of calculation is the older one, based on the chemical equation, as was explained in connection with each example.

This table also gives the full names of all the elements in alphabetical order, while the other contains only the more important elements classified in the alphabetical order of their symbols. It also contains the atomic weights (based on $O = 16$) of all the elements, thus enabling one to calculate (by means of the formulas in the last line of the first table) any of the electrochemical equivalents or their derivatives of the elements not included in the first table.

The following few general rules concerning valencies may often be found useful: The valency expresses the number of bonds uniting an element with others in a compound. These bonds (as far as electrolysis is concerned) are negative and positive. For each negative bond of an element in a compound, there must of necessity be a corresponding positive bond of some other element. Each of these negative bonds corresponds to a charge of $-96{,}540$ coulombs (or 26.82 ampère hours) of electricity per uni-valent gram ion, and each positive bond to $+96{,}540$ coulombs. A change of valency implies a disappearance or appearance of positive and negative bonds, and hence a passage of electricity corresponding in amount to these charges set free or taken up.

An atom of oxygen is assumed to always have two negative bonds; hydrogen always one positive; chlorine (in chlorides) always one negative; SO_4 (in sulphates), always two negative; NO_3, always one negative; ClO_3, always one negative. In metallic solutions, where the metal is the base, its bonds are positive, while those of the radical are negative. Elements in their uncombined form (as deposited metals or free gases) are assumed to have no bonds. These few rules, together with the rule that all the positive and negative bonds must always add to zero, will enable one to find the valencies in most of the usual electrolytes.

This conception of negative valencies, which makes it possible to apply these rules concerning the change of valency to all cases, appears to have originated with Prof. Otis C. Johnson. He did not, however, apply it to electrochemical calculations. The conception of the change of valency as a basis of electrochemical calculations is the same thing, in different words, as the conception of charges received and given off by the ions at the electrodes, which is so frequently used in connection with the dissociation theory. But the use of the table as above described avoids the lengthy calculation involving the ionic charge 96,540, as this constant is already included in the figures given in the table.

ALUMINIUM AS A REDUCING AGENT IN METALLURGY.

By George P. Scholl.

The fact that metallic aluminium, under proper conditions, reduces many of the other metals from their compounds has been known a long time ago. No less a personage than the illustrious Friedrich Woehler, the discoverer of aluminium, tried, in 1857, to produce chromium from its chloride by means of metallic aluminium, and succeeded in obtaining a chromium-aluminium alloy. Numerous attempts have since been made by various investigators—among them Michel, St. Claire-Deville, the brothers Tissier and last, not least, Messrs. Greene and Wahl in Philadelphia—to utilize this reducing property of aluminium for practical purposes. But the stumbling block in the path of these experimenters was the fact that the reduction only takes place at a high temperature, and when this temperature has been reached it proceeds with explosive violence. It was left to Dr. Hans Goldschmidt,

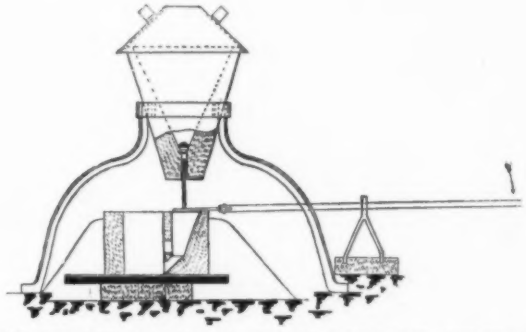


FIG. 1.—SECTIONAL VIEW OF CRUCIBLE ARRANGED FOR TAPPING.

Essen, Germany, to find out the means by which to temper the violence of the reaction and to evolve what is now known as the Goldschmidt process.

In the course of his researches, prompted by the firm of Friedrich Krupp, of Essen, and undertaken with a view to find a process for the manufacture of pure chromium and manganese, he discovered that, in order to have the reaction take place, it was only necessary to start it at one point of the mixture. As the reduction of metallic compounds by aluminium is an exothermic reaction, and takes place with a considerable evolution of heat, the heat liberated at that one point is sufficient to raise the adjacent portions of the mixture to the temperature of reaction, and so on, until the reaction has propagated itself throughout the entire mixture. This, then, was the keynote to a successful application of the aluminium reduction process in practice, but there remained a very serious

problem to be solved yet, namely, to find the best method to start the reaction. After many fruitless attempts, it was finally discovered that substances like the peroxides, chlorates, etc., which easily yield up their oxygen, could be successfully used for this purpose. It requires comparatively little heat to bring them to the point of reaction, and the heat given out thereby is sufficient to start the ignition of the mixture to be reduced. Barium peroxide has been found most satisfactory, and is most generally used.

As a typical example of the method of procedure, it will suffice to describe the reduction of metallic iron from its oxide by means of aluminium. The chemical equation, according to which the reaction takes place, is exceedingly simple, namely, $Fe_2O_3 + 2Al = Al_2O_3 + 2Fe$. The aluminium acts just like

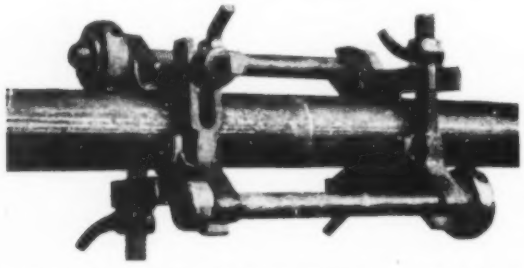


FIG. 2.—PIPES CLAMPED TOGETHER BEFORE THE MOLD IS PUT AROUND.

the carbon in the ordinary reduction process, but while the products of combustion in the case of carbon (carbon monoxide and dioxide) are gaseous, the product of combustion in this case is a solid, which, however, becomes fluid through the heat of reaction. The oxide of iron is mixed with powdered aluminium in the right proportion, and introduced into a crucible lined with magnesia or with material obtained from a previous fusion. The mixture cannot be treated in an ordinary crucible, as the alumina, being of a strong basic character, would, at the high temperature developed in the process, immediately combine with the silica of the crucible and destroy it. Ordinarily the mixture would be very hard to ignite, as it can be thrown into an ordinary fire, and even upon molten cast iron, without burning. In order to set off the mixture, a

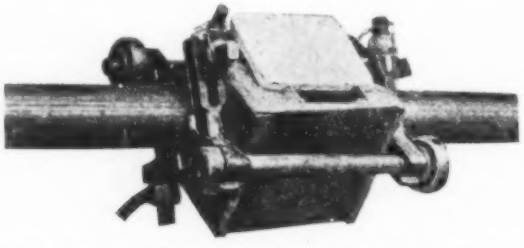


FIG. 3.—HORIZONTAL PIPES WITH MOLD, READY FOR POURING.

small quantity of ignition powder (barium peroxide and powdered aluminium) is put in a small heap on top of the mixture, and is ignited by means of a storm match or by touching it with a red-hot iron rod. The reaction propagates itself quickly through the whole mixture, with the result that in a few seconds the whole charge is a mass of white-hot fluid material. The contents of the crucible have separated into two layers, the molten metal, reduced by the aluminium, being at the bottom and the molten Al_2O_3, corundum, above it. That the heat developed during the operation is very great can be seen from the fact that the alumina, the melting point of which lies at about 1,900° C., is liquefied. The temperature of the molten mass in the interior of the crucible has been estimated at 3,000° C. (5,400° F.).

In order to understand the remarkable development of heat in this process, it has to be considered thermo-chemically and a comparison made between the energy density in the crucible and the energy density obtained in other sources of high temperature—for instance, the electric furnace. Starting from the reaction, $Fe_2O_3 + 2Al = Al_2O_3 + 2Fe$, there are required, theoretically, .484 kilograms aluminium for the production of 1 kilogram of metallic iron, furnishing .91 kilograms of alumina. Assuming the heat of combination of 1 kilogram Al to Al_2O_3 as 7,140 calories, as determined by Dr. Straus, of Friedrich Krupp, in Essen, there are set free in the above reaction $.484 \times 7{,}140 = 3{,}455.76$ calories. These calories have to furnish the heat necessary for the reduction of the iron, the heating of the iron to its melting point and the heating of the resulting alumina to its melting temperature.

Assuming the average heat necessary for the reduction of Fe from Fe_2O_3 as 1,768 calories, 1 kilogram of Fe will require 1,768 calories. If we take the melting point of wrought iron at 1,600° C., the average specific heat of wrought iron between 0 and 1,600° as .19 and the latent heat of fusion as 33 calories, the iron, in order to be melted, requires 337 calories. Finally, taking the melting point of alumina as 1,900° C., its specific heat as .2173 and its latent heat of fusion as 50 calories, we get 425.71 calories required for the melting of the alumina. The balance, therefore, neglecting the loss by radiation, is as follows:

Heat generated			
By the reaction of .484 kg. aluminium			3455.76 cal.
Heat required			
For the reduction of 1 kg. Fe from Fe_2O_3	1768	cal.	
For the fusion of the metallic iron	337	"	
For the fusion of the alumina	425.71	"	2530.71 cal.
			925.05 cal.

There is, therefore, a surplus of heat of 925.05 calories, and, as 1 kilogram of the mixture of oxide of iron and aluminium

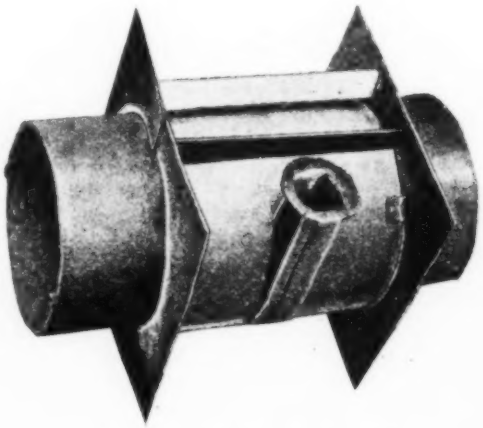


FIG. 4.—MOLD FOR PIPE OVER 5 IN. WIDE.

gives practically ½ kilogram of iron, there are about 450 calories of heat furnished for each kilogram of the mixture. In order to understand why such a relatively small amount of heat could cause the raising of the mixture to such a high temperature as 3,000° C., we must recall the fact that the reaction takes place with great velocity, and that, furthermore, the product is not a gas, as in the case of carbon, for the gasification of which a large amount of the energy has to be expended, but solid, and that the whole energy of the reaction is preserved, as it were, in the crucible.

The average time of reaction of 1 kilogram of the mixture is about one or two seconds, and with large quantities this time is still considerably reduced. Supposing that only 300 calories in one second are developed by the reaction of 10 kilograms of the mixture, the work done would equal $300 \times 425 = 127{,}500$ meter kilograms, or 1,700 horse-power seconds, or 1,149.5 kilowatt seconds, nearly equaling the effect in one second of an arc lamp of 30,000 ampères at 40 volts.

The data given above are taken from a recent paper read by Dr. Goldschmidt before the Society of German Chemists (*Zeitsch. Anorg. Chemie*, 1902, p. 699), where he also gives a comparison between the energy density developed in his process and in the electric furnace, which is of considerable interest to electrochemists. The energy density is calculated in ergs per cubic centimeter. As calculated above, there are available 450 calories for each kilogram of the mixture, and when 10 kilograms react in fifteen seconds, and occupy a space of 3,500 c.c. after the reaction has taken place, there are in 1 c.c. 0.0857 calories = 36.42 mkg. As 1 mkg. = 98,100,000 ergs, there are in one second in one c.c. 3,572,802,000 ergs. In an electric furnace like that of Stassano, where the heat is generated by a powerful arc, heating a space of about 1 cubic-meter, with an expenditure of energy of 500 horse-power, the energy density is 500 horse-power = 37,500 mkg. in 1,000,000 c.c. per second, consequently per second per c.c. 0.0375 mkg. = 3,678,750 ergs, or nearly as 1 to 1,000 as compared with the Goldschmidt crucible. The following table gives a comparison with the energy density of a 500 horse-power calcium carbide furnace:

Time of reaction	Amount of mixture.	Volume of the Reaction product	There are generated		Density		Relation between the energy-densities	
			Total calories	Available calories	of total energy	of available ccm. pco sec.	(a). Carbide furnace to total quantity of heat in crucible, 1:188	(b). Carbide furnace to available heat, 1:5
15 sec.	10 kgs.	3,500 c.m.	17,278.8 cal. = 7,343,490 mkg.	4,500 cal. = 1,912,500 mkg.	0,33 cal. = 140.25 mkg. = 13,758,525,000 ergs.	0.857 cal. = 3.64 mkg. = 357,084,000 ergs.		
1 sec.	Carbide generated in 500 hp. furnace, 0.173 kg.	Volume of melting zone 5,000 ccm.	500 hp. = 37,500 mkg.		0.75 mkg. = 73,575,000 ergs.			

Of the many applications which the process finds, one of the most important is the production of pure chromium and manganese. Chromium, as is well known, is a most valuable constituent of steel, but until it was made possible to obtain it by the Goldschmidt process it had to be manufactured either in crucible furnaces or in the electric furnace by reducing chrome iron ore with carbon. This, of course, gave not a pure material, but a so-called ferro-chromium, containing about 63 per cent. of chromium and a large amount, up to 12 per cent., of carbon. When this material was introduced into steel, the carbon which it contained added itself to the percentage of carbon already present in the steel. It was therefore impossible to produce a chromium steel low in carbon and at the same time containing an appreciable amount of chromium. The pure metal is now produced by the Goldschmidt process in large and increasing quantities, and finds a number of applications in the manufacture of special steels, as well as in the manufacture of guns, shells and armor plate.

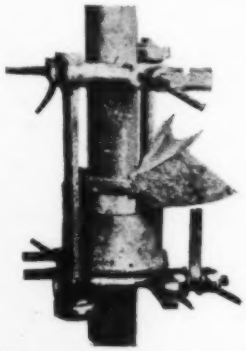


FIG. 5.—MOLD WITH LATERAL POURING FUNNEL FOR VERTICAL PIPES.

The reduction of chromium is very simple, taking place according to the equation $Cr_2O_3 + 2Al = Ae_2O_3 + 2Cr$. The mixture of finely-powdered aluminium and chromic oxide is made in the usual way, and the reaction started by igniting the charge with the ignition powder. The metal in a fused condition collects at the bottom of the crucible, with the corundum slag above it. The process is a strong rival of the electric-furnace process for the production of ferro-chromium, especially as the latter is not of such uniform composition as regards the carbon as is absolutely necessary where alloys of a definite composition have to be obtained. It is also probable that the process will cut short the efforts to produce pure metallic chromium by electrolysis.

Manganese is also produced of a high degree of purity, up to 99 per cent., the impurities being mostly iron and silicon. It is used to a large extent for copper-bronze and nickel castings. An alloy of 70 per cent. manganese and 30 per cent. chromium is used for the manufacture of special copper alloys, the so-called copper-manganine. Pure manganese is also used in the steel industry for the production of special steels high in manganese, containing up to 12 per cent. of that metal.

Ferro-titanium is another product of the process. The mixture of aluminium with the titanium compound is inflamed by contact with molten cast iron, acting in this way different from the mixture of oxide of iron and aluminium, which is only ignited at the temperature of molten steel. This behavior is made use of for alloying titanium with cast iron by throwing the mixture right on the bath of molten metal. An alloy of ferro-titanium is formed with the evolution of considerable heat, which combines directly with the cast iron. The mixture is added in quantities of ½ to 1 per cent., and, within these limits, has a very beneficial effect in making the cast iron finer grained, less brittle and more thinly fluid. In steel castings,

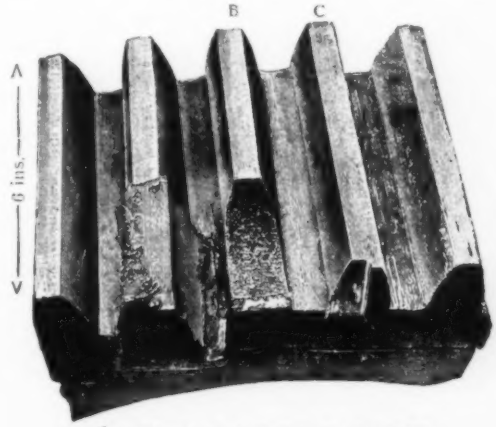


FIG. 6.—SECTION OF A WHEEL FOR REPAIRING.

considerably smaller additions of titanium are sufficient to produce solid castings. The cast iron on which the titanium mixture is thrown has to be sufficiently hot, otherwise the ignition will not take place and some of the metallic aluminium may alloy with the iron, producing unfavorable results.

One of the most interesting of the applications of the process ,and probably the most widely used at the present time, is the employment of a mixture of oxide of iron and aluminium, in certain proportions, for welding and repairing purposes. This mixture is called by the inventor "Thermit." Two methods can be used for the welding, the first one depending merely on the utilization of the enormous heat which is developed during the reaction for the heating of the pieces to be welded, and in the second the welding is accomplished by means of the molten, white-hot iron produced. The first one of these methods is chosen where it is desired to weld pipes or pieces of iron together with their butt ends. The butts are fitted well together, and the ends to be welded are cleaned with a file or emery paper. They are then clamped firmly together, and a mold made from strong sheet iron is put around them. In pipes over 5 inches diameter, the pipe has to be completely surrounded by a mantle, with pouring funnel, and a large hole has to be provided for the exit of the air. Pipes can be welded in any position, only the mold has to be

changed to suit the purpose. Several arrangements are illustrated in the accompanying figures. The necessary amount of thermit is then brought to reaction in a crucible, and the contents of the crucible are poured into the mold. When the molten corundum, which flows out first, comes into contact with the cold pipe and the metal of the mold, a layer of chilled corundum forms on them, which cannot be melted any more by the following corundum or molten metal. If the latter would come into contact with the unprotected pipe, it would melt it through at once. The molten mass quickly brings the iron to the welding heat, and then the set screws, which hold the pieces of pipe, are drawn together and the pipes thus pressed closely against each other.

With vertical pipes, the mixture has to be quickly removed, because the ring of metal on the bottom of the mold might stick to them. With horizontal pipes, this is not necessary, and it is better to let the weld cool slowly. Square, round or shaped iron can be welded in the same way. Exact specifications have been prepared for welding pipes from ¾ inch up to 6½ inches diameter, giving amount of thermit necessary, diameter of the mold, etc.

It is important to note that this method of welding is also applicable for coils, which can be welded *in situ* after the parts have been previously bent to the desired form. The welding by this method is of such excellence that the welded part is stronger than the other parts of the pipe. One reason for this is the absolute exclusion of the air during the welding

FIG. 7—RAIL WELDING BY THE GOLDSMITH PROCESS.

process. The welding is, further, absolutely equal in all cases where the same quantity of thermit has been taken, and consequently exactly the same amount of heat has been generated.

The second method, in which the metallic iron produced in the reaction is utilized for uniting the objects to be welded, is carried out in a crucible, shown in cross section in the illustration. The conical crucible has a hole in the bottom, which, during the operation, is closed by a small iron disk, on which is placed a thin layer of fine sand. When the reaction is finished, the small iron disk is pushed up by means of a lever and the contents of the crucible run into the mold. If no layer of sand is put on the iron disk, it will melt through before all the thermite has entered into reaction. The molds have, of course, to be thoroughly dried. The iron produced in the reaction is a very pure wrought iron, specimens showing a composition of C = .10 per cent., Mn = .08 per cent., Si = .09 per cent., S = .03 per cent., P = .04 per cent., Cu = .09 per cent. and Al = .07 per cent. On account of its high temperature, of about 3,000° C., when poured on an object of iron, it softens its surface and welds itself firmly to the object. This method of welding has been used a great deal for welding tramway rails together, in order to avoid the various troubles arising from bad connections between the rails. The rails can be united either by butt-welding them or by simply casting a connection around their ends. The equipment necessary for welding rails is shown in an adjoining figure.

Another important feature of the process is the ease with which it can be applied to carrying out repairs in all kinds of castings. An example of this is shown in the illustration, where the teeth of a gear wheel have been repaired. The tooth on the left shows the repaired tooth before the surface is planed off; the one on the right is partly planed off, and the center tooth is left unrepaired, to show the appearance of the break. It is thus possible to save valuable castings which otherwise would have to go to the scrap heap. The process is also well adapted for the patching up of faulty castings, and, in fact, has such a wide applicability in many instances which are daily encountered in iron foundries and mills that any progressive manager ought to familiarize himself with it. Broken shafting can be welded and repaired in place, and it is stated that even ships' propeller shafts can be repaired at sea, as the apparatus for the purpose is very simple and no large quantities of molten material have to be transported. Instances like this might be multiplied, but they will readily suggest themselves to anyone familiar with foundry and mill work. The increasing application which the process has found in the leading iron and steel works abroad speaks volumes for its practical success.

Altogether, the process is a most interesting one to metallurgists, and has attracted considerable attention. It has not been a haphazard invention, but the result of a painstaking research by a man of broad scientific training, and the inventor has to be congratulated on his success in solving a problem which has baffled experimenters for a long time.

The writer wants to express his thanks to Mr. C. E. Schulz for valuable information on special points in connection with this subject.

WHY THE E.M.F. OF THE DANIELL CELL CHANGES WITH THE DENSITY OF THE SOLUTIONS.

By Prof. Henry S. Carhart.

In my paper on "A Thermo-Electric Theory of Concentration Cells," read at the Niagara meeting of the American Electrochemical Society, I ventured to give a new explanation of the well-known dependence of the E.M.F. of the Daniell cell on the concentration of the two solutions. The explanation is based on the fact brought out in my paper that the thermo-electromotive force between a metal and a solution of one of its salts increases with the concentration of the solution. The relation between the two is shown in Fig. 4 of my paper, as published in Vol. II of the Transactions of the Society. The thermo-electromotive force is directed from the solution to the metal. Since this is in the opposite direction to the E.M.F. of the cell itself at the zinc electrode, an increase in the thermo-electromotive force at the zinc lowers the E.M.F. of the cell. At the copper electrode, on the other hand, an increase in the thermo-electromotive force increases the E.M.F. of the cell. Now when the concentration of the zinc sulphate solution is increased, the counter E.M.F. of thermal origin at the zinc electrode also increases, and, therefore, the E.M.F. of the cell decreases. Similarly an increase in concentration of the copper sulphate solution increases the thermal E.M.F. at the copper electrode, and this increase adds to the E.M.F. of the cell.

In the October number of this journal Prof. Jos. W. Richards has indirectly called in question my explanation of the phenomenon under discussion by offering another one, namely, the variation in the heat of formation of zinc and copper sulphates, in aqueous solution, with the concentration of the solutions formed. The heat of formation of both sulphates decreases as the concentration increases. The more dilute the solution, the greater the heat of formation. The same relation holds in the case of zinc chloride solution. This fact is brought out in the

classical researches of Jahn, which supported and confirmed the famous Gibbs-Helmholtz equation for the E.M.F. of a voltaic cell. If, therefore, the zinc is dissolved in a more concentrated solution, the formation heat of the zinc salt is less, and the E.M.F. of the cell is diminished. If, on the other hand, the copper is deposited from a more concentrated solution, in which the heat of formation of the copper salt is less, the value of the heat energy transformed in the cell is increased, and its E.M.F. is also increased.

The criticism of Professor Richards has led me to make a few measurements. The results are certainly interesting, and to my mind they are decisive as to the competency of the explanation which I gave in my Society paper. I say "competency," because I do not claim that this explanation excludes others when the subject is approached from a different point of view.

I set up a small Daniell cell of the two-legged variety, connected by small lateral tubes and a short piece of rubber tubing, the same as I have heretofore often used in my measurements of thermo-electromotive forces. In the rubber tube was a short piece of pipe stem to serve as a porous partition. The zinc side of the cell contained first a one-sixteenth normal zinc sulphate solution, and subsequently a normal solution. The E.M.F. was carefully measured in both cases by means of a Wolff's potentiometer or compensation apparatus, and the difference was 0.021 volt at 20° C. The value calculated from the difference in the two thermo-electromotive forces at the zinc surface alone would be somewhat higher. For the 1-16 normal solution the thermo-electromotive force per degree C. is 0.0007 volt; for the normal solution it is 0.0008 volt. The difference multiplied by the absolute temperature gives the calculated value of the variation of the E.M.F. when the one solution is substituted for the other in a Daniell cell. The product is 0.029 volt. The thermal electromotive forces are therefore ample to account for the observed variation in the E.M.F. of the cell. In this calculation I have not taken into account any small thermal E.M.F. at the junction of the two solutions.

The very interesting fact in this connection is that the change in E.M.F. of the Daniell cell when the one zinc sulphate solution is substituted for the other is the same as the E.M.F. of a concentration cell set up with zinc electrodes and the two solutions. A little consideration will serve to show that this should be the case. Suppose two similar Daniell cells set up with the same concentrated copper sulphate solution, one with the 1-16 normal zinc sulphate, and the other with the normal solution. Suppose, further, that the two are connected in opposition. The potential difference would then be the difference in E.M.F. of the two cells. This combination would be like a zinc concentration cell with the two halves connected by a tube containing copper sulphate separated from the zinc sulphate on the two sides by porous partitions. In confirmation of this view, I joined two such Daniell cells in opposition, and added in series with them a zinc-sulphate concentration cell set up with the same solutions, 1-16 normal and normal. The concentration cell was turned so that its E.M.F. opposed that of the two Daniells. As anticipated the three cells balanced within 1-1000 volt. A separate measurement of the two Daniells in series and of the concentration cell gave the same result.

Hence, any competent explanation of a simple concentration cell is directly applicable to explain the variation in the E.M.F. of a Daniell cell with a change in concentration of the solutions.

Ideally a concentration cell is one containing no internal chemical energy to be transformed. Such is the case when the solutions are so dilute that they generate no heat when mixed. The heat of dilution is then negligible. The first term in the Gibbs-Helmholtz equation is then also negligible, and the second one, involving the absolute temperature and the temperature co-efficient is the sole expression of the E.M.F. But the temperature co-efficient is the sum of all the thermo-electromotive forces at the several junctions in the cell, all taken with their proper sign. All this rests on the surest experimental facts, and this constitutes the thermo-electric theory of a concentration cell. Such a cell converts heat into electrical energy. In the limit, when there is no internal chemical energy, all the heat is absorbed from the surroundings. On the more dilute side, where the current flows in the opposite direction to the thermo-electromotive force, the heat generated is the combined product of the absolute temperature, the temperature co-efficient or thermo-electromotive force at that electrode, and the quantity of electricity passing. On the other side, where the current flows in the same direction as the thermo-electromotive force, the heat absorbed is the same combined product; but the latter is larger than the former because the thermo-electromotive force is greater. In the measurements which I have made it is enough greater to account for the whole E.M.F. of the cell. Hence the heat of solution must be negligible, or else the necessary heat absorbed comes in part from the dilution. This point is capable of experimental determination by one of the methods used by Jahn in his well-known researches.

The explanation applicable to the concentration cell may be carried directly over to the Daniell cell and applied to explain the change of E.M.F. due to a change of concentration.

The foregoing measurements show that for the concentrations used the E.M.F. of the concentration cell is the same as that of the two Daniells in opposition. This result is not in agreement with the conclusion of Nernst that the E.M.F. of the concentration cell is to the difference of the two Daniells as the ionic velocity of the anion is to the sum of the ionic velocities of the anion and the cation. (See Jaeger's *Die Normalelemente*, p. 29).

TWO GERMAN PLANTS FOR STERILIZING WATER BY OZONE.

The first two German plants in which electrically produced ozone is used as a sterilizing and oxidizing agent in connection with commercial water works, were opened last autumn in Schierstein, near Wiesbaden, and in Paderborn. That ozone is well adapted for water sterilization, being a powerful destroyer of organic matter, both vegetable and animal, is well known and requires no longer proof by practical experiments. But the all-important question is whether the cost of this

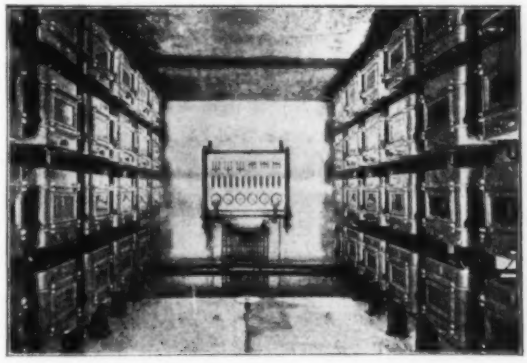


FIG. I—OZONIZER ROOM.

method is not prohibitive. This question, however, can be decided only in actual practice on a commercial scale, and for this reason all facts published on commercial plants must be of interest. A method used in two Dutch plants was described in ELECTROCHEMICAL INDUSTRY, September, 1902, Vol. I, pages 31 and 32; in these plants the Vosmaer-Lehret system is used. The two German plants which will be described in the following, were installed by the Siemens & Halske Co. of Berlin.

The plant at Schierstein was installed to the order of the

municipal authorities of the city of Wiesbaden, and is designed to sterilize 250 cubic meters (66,000 gallons) of water per hour as a maximum, as stated in recent articles in *Schilling's Jour. f. Gasbel. u. Wasserversrs,* 1902, No. 40, and in *Zeit. f. Elektrochemie,* 1902, No. 43. But this maximum output is required only for occasions when exceptionally large amounts of water are needed, while in the average only one-half, *i. e.*, 125 cubic meters (33,000 gallons) are sterilized per hour. The other half of the plant serves in general as reserve; the plant is therefore divided into two independent halves, but the apparatus of one-half may be worked in connection with the other half; for instance, each set of dynamos may be easily switched over from one-half to the other.

The dynamos installed give current for driving the pumps and also current for the transformers. The transformers are wound for 180 volts primary and 8,000 volts secondary, the secondary windings being connected to the ozonizing apparatus. The ozone produced is then driven by fans into the sterilizing towers, in which the ozone rises upwards and comes into contact with the water flowing down; the water is thus sterilized and flows off into a reservoir.

In the ozonizer room there are 48 ozonizers at both walls of the room, as shown in Fig. 1. As noticed before the whole

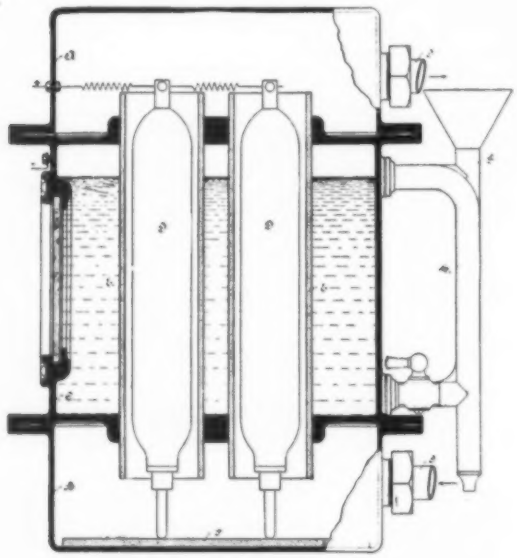


FIG. 2—OZONE APPARATUS.

plant is divided into two separate halves, and each half contains therefore 24 ozonizers; these are divided into three series, each of eight ozonizers, and each such series of eight apparatus is connected to the 8,000-volt secondary winding of a transformer. One such series of eight apparatus gives the ozone required for one sterilization tower. The ozonizers are of the Siemens tube type (glass at the one hand and metal at the other hand), one pole being earthed on account of the method of cooling the discharge surface with water. The ozonizer tubes are shown in Fig. 2, in which A and B are the upper and lower covers, while C is the middle part of the ozonizers, DD are connected to the positive pole, G and H are the tubes for the cooling water, and JJ are the tubes for the air.

The connections to the positive pole (the pole which is not earthed) are well protected, so that it is impossible for the attendants to touch them. Eight ozonizing tubes are contained in an iron box, the upper, lower and front sides of which are provided with thick glass windows. The ozonizer room is generally kept dark, and the attendant who enters it sees at once from the blue light passing through the glass windows of the ozonizer boxes whether the apparatus is working satisfactorily. As all metallic parts connected to the 8,000-volt pole are entirely protected, the attendant can only touch those parts which are connected to the other (earthed) pole, and there is no danger.

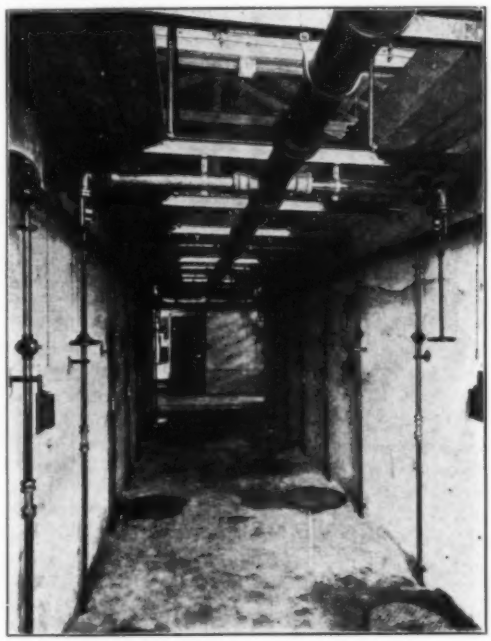


FIG. 3—STERILIZING ROOM.

The sterilizing room which is shown in Fig. 3, contains two series each of four towers of brick. Each tower is divided into four sections by two partition walls perpendicular to one another. A cross section of such a sterilizing tower which is about four meters (13 feet) high, is shown in Fig. 4. As

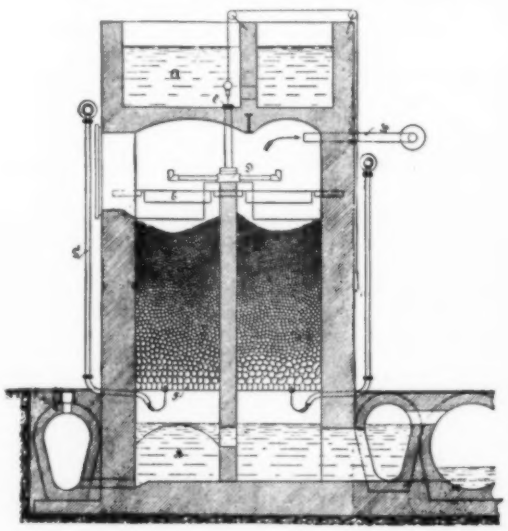


FIG. 4—CROSS SECTION OF A STERILIZING TOWER.

will be seen the tower is filled up to about two meters (6½ feet) with coarse-grained gravel through which the water is trickling down, meeting on its way the uprising ozone current. C is a device for stopping the run of water automatically whenever the operation is interrupted in some way. Through

each full tower (*i. e.*, through its four sections together) 42 cubic meters (11,100 gallons) are flowing downwards per hour, while in the same time 80 cubic meters (2,800 cubic feet) of ozonized air pass upwards. A is the basin containing the not-sterilized water, B the basin containing the sterilized water, EE are screens, G the tube through which the ozonized air is introduced and H the tube through which the air flows off.

Accidents can occur when the operation of the electric apparatus should be interrupted or the introduction of ozonized air to the sterilizing towers should cease, for some reason. Whenever this should happen very simple and reliable automatic devices are provided which prevent a further supply of not-sterilized water to the sterilizing towers.

For the operation of each half of the plant (sterilizing 125 cubic meters or 33,000 gallons of water per hour) 50 horse-power are required, of which 27 horse-power are used for the ozonizers, 22 horse-power for the pumps and 1 horse-power for various purposes.

The cost of the process at Schierstein is 0.35 cent per cubic meter of water, 0.1 cent being the cost of coal required for the operation of the ozonizing apparatus. To this must be added a charge for interest and amordization, which is about 0.15 cent, so that the total cost per cubic meter is 0.5 cent. It is to be considered that at the Schierstein plant power is required for operating pumps which is not necessary for any ordinary ozonizing plant.

Tests of the sterilized water, made by Prof. Proskauer and Dr. Schueder, and also other tests made in the Fresenius Institution, showed that the sterilization process by means of ozone is in every way successful, so far as the results—*i. e.*, the annihiliation of germs and bacteria—is concerned. The process is therefore well adapted for the purification of drinking waters.

A month after the Schierstein plant, the Paderborn plant

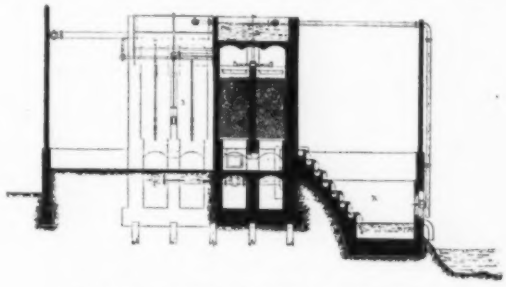


FIG. 5—STERILIZING TOWERS AT PADERBORN.

was opened. Its installation is exactly the same as that of the Schierstein plant, with the only exception of the sterilizing towers. They are illustrated in Fig. 5; the sterilized water is flowing off in form of cascades, so that the ozone dissolved in it is given off. The cost of sterilizing one cubic meter of water is in this plant about 0.4 cent, including charge for interest and amortization.

SYNOPSIS OF ARTICLES IN OTHER JOURNALS.

A Summary of Articles on Electrochemistry and Allied Subjects Appearing in American and Foreign Periodicals.

BY CARL HERING.

INDUSTRIAL ELECTROCHEMISTRY.

Conversion of Amorphous Carbon into Graphite.—Those interested in the artificial production of graphite will find an interesting summary of the systematic work done by various investigators, in a recent paper by FITZGERALD, before the Franklin Institute, and published in the journal of that society for November. Much work has been done in this direction, notably by Despretz, Berthelot, Moissan and Acheson. By the Acheson process the conversion of amorphous carbon into graphite is complete according to Berthelot's definition of graphite, as that form of carbon which on oxidation at low temperatures yields only graphitic oxide. The density is thereby increased considerably, the mean value of densities of six electrodes before graphitizing being 1.90, and after graphitizing 2.19. The electric conductivity is at the same time greatly increased, Lincoln having found the resistance of one cubic inch of an amorphous carbon electrode to be 0.00124 ohm and that of one cubic inch of graphite electrode 0.00030 ohm, that is about four times the conductivity. The purity of the graphitized carbon is greater than that of the amorphous from which it is made, for a greater or less quantity of the impurities is volatilized, the final purity depending on the temperature to which the carbon has been raised and the time expended in heating. A specimen of anthracite coal was analyzed and found to contain 5.783 per cent. of ash. After prolonged heating and conversion into graphite the latter was found to contain only 0.033 per cent. of ash. In summarizing the more important work done by the various investigators, the author remarks that their results are by no means in agreement. Despretz in his experiments was endeavoring to show that carbon can be fused, welded and volatilized, and thought he had done so. Moissan, however, in his experiments never found any sign of fusion, and concludes that vaporization occurs without previous fusion. In some of his experiments at least, Despretz probably mistook the formation of fusible carbides for fusion of carbon. Despretz's conclusion that any carbon becomes proportionately softer as it is heated for a long time to a high temperature, is incorrect; for instance, the hardness of the ordinary manufactured carbon is increased by prolonged baking at a very high temperature; and some forms of anthracite coal may be so greatly hardened by heating for some time to a high temperature out of contact with air, that they will readily scratch glass. Berthelot's definition of graphite, as given above, is perfectly satisfactory from the chemical point of view, but it is not always satisfactory in practice, for example some forms of carbon which come under his definition do not mark paper. The conclusion to be drawn from a comparison of Berthelot's and Acheson's researches seems to be that while all true graphites yield graphitic oxide, all bodies yielding that compound are not necessarily graphites suitable for practical purposes. In view of the fact that various kinds of hard and soft graphites produced by artificial means are now being put on the market, and that varieties of amorphous carbon (notably retort carbon) are also sold under the name of graphite, the author thinks it would be advisable to revise the nomenclature of carbons, reducing it to a more rational and practical form free from all ambiguities. The most interesting of Moissan's methods of transforming amorphous carbon into graphite, as compared with the commercial method, is the conversion by a simple elevation of temperature. While his investigations show clearly that heat has a most distinct effect in bringing about the polymerization of both carbon and graphite, yet, in view of Acheson's work on the remarkable part played by various carbide-forming sub-

stances, in effecting the transformation of amorphous carbon into graphite, none of Moissan's experiments are rigidly conclusive in demonstrating that the change is effected solely by elevation of temperature.—*Jour. Frank. Inst.*, November.

Electrolytic Alkali Industry.—To the literature on alkalies J. B. C. Kershaw contributes another article in the Lond. *Elec.*, December 12th, which is the conclusion of his former illustrated one. He discusses the electrolytic alkali industry in the United States. He makes brief remarks on some American companies, but seems to give nothing new, nor is his review complete. Some general remarks on the financial conditions of the electrolytic alkali industry and the rivalry of the older Le Blanc process are added. It is said to be proved that a well-equipped Le Blanc alkali plant, using the Deacon process for decomposing its hydrochloric acid, can produce bleach at present at a cost below $17.50 per ton. The fall in the selling price of bleaching powder, while it will seriously curtail the profits of the Le Blanc works, will therefore not cause actual loss to the manufacturer, and therefore continued competition from this quarter must be expected by the electrolytic alkali companies. The author also gives data on the cost of the electrolytic process and finally reaches the conclusion that the total cost of 1 ton of 72 per cent. of caustic soda and 2.1 tons of 35.0 per cent. bleaching powder, by the best electrolytic processes, is about $70. The present selling value of the above amounts of these chemicals is, however, $110, and the 1903 value, when the drop in the value of bleach will have become effective, is $86.25. The prospects of the electrolytic alkali works are therefore not as hopeless as their rivals are disposed to believe; and although some of the companies may fail during the approaching period of competition, it is probable that the stronger ones will survive the ordeal, and that they will be benefited by this trial of strength with the old Le Blanc works.

The Lond. *Elec.*, December 9th, contains an official communication from the electrochemical electrolytic alkali works at Bitterfeld, Germany, to the effect that Kershaw's statement that the Aussig bell process is being used at one of the Bitterfeld works, is wrong.

Statistical.—Among the annual statistical information to be expected in this month is an article in the *Eng. and Min. Jour.*, January 3d, by Schnattenbeck, on the chemical and allied mineral trades in 1902. In America rapid progress is being made in the manufacture of chemicals, notably those which have heretofore been considered entirely European products. The domestic production of alkali is growing steadily, and as prices are low and the quality of alkali good, imports have fallen over 60 per cent. in two years. Manufacturers of electrolytic caustic soda are proving hard competitors to sellers of the old process article, and imports are suffering severely from this competition. The consumption of bleaching powder is great, as is shown by the large imports and increased domestic production; prices are very low and "in fact, the prices accepted on new contracts are so low that it is impossible for the older works to compete with the modern plants employing electrolytic processes." The domestic consumption of bleaching powder is now about 75,000 or 80,000 tons a year, of which our own works contribute an increasing quantity, while Great Britain and Germany furnish the bulk of the imports. A feature in the trade was the appearance of the new electrolytic bleach made by the Solvay Process Co. of Belgium. Notes are also given on bicarbonate of soda, sal soda, chlorate of potash, chlorine gas, copper sulphate, sulphuric acid, nitric acid, muriatic acid, oxalic acid, carbon dioxide, brimstone, pyrites, alum, copperas, cyanide, cryolite, bromine, barytes, arsenic, zinc dust, bichromates, nitrate of soda, sulphate, ammonia and potash salts.

The same journal contains another by Struthers, on the production of minerals and metals in the United States during 1902. He gives a preliminary statistical table of the output in the United States during 1902. The grand total of the value of metallic and non-metallic substances produced in the United States from domestic ores during 1902, was $1,360,344,147, as compared with $1,198,938,697 in 1901, an increase of 13 per cent. for the year. The total value of metals was $569,149,785, as compared with $496,155,923, an increase of 15 per cent. The value of the production of non-metallic substances was $886,694,362, as compared with $796,411,855, an increase of 12 per cent. The production of aluminum was 7,300,000 pounds, valued at $2,284,590 (against 7,150,000 pounds, and $2,238,590 in 1901). The copper produced in 1902, was 669,855,006 pounds, valued at $78,630,453 (against 609,173,212 pounds and $87,300,515); 358 ounces troy of platinum were produced from domestic ores, and 674 ounces were recovered from South African ores; the quantity of platinum imported during the first eleven months of 1902 was 6,467 pounds (apparently avoirdupois), valued at $1,766,869. The output of zinc was 158,447 short tons, valued at $14,380,650. The output of carborundum was 3,800,000 pounds, valued at $324,058. The output of artificial graphite was 2,351,491 pounds, valued at $111,251. The quantity of sodium salts manufactured in this country was 528,000 tons, valued at $9,477,600. There are also special articles on antimony in 1902; copper, gold and silver, lead, nickel, platinum, tin, zinc, iron and steel, coal, and on progress made in metallurgy at various places.

THEORETICAL AND EXPERIMENTAL.

Electrolytic Conductivity.—Judging from the amount of matter recently published on this subject, it has received considerable attention lately, from various standpoints. With reference to theoretical questions, more especially the testing of the validity of the Nernst-Thomson rule, Kahlenberg and Schlundt have recently made some interesting investigations on the solubility, electrolytic conductivity and chemical action in liquid hydrocyanic acid, published in the *Jour. Phys. Chem.* for October. They are of special interest on account of the high dielectric constant of this solvent, thus making possible an exact examination of the Nernst-Thomson rule. The facts are, that while some salts dissolved in liquid HCN conduct electricity better than in water, many others conduct much worse than in their corresponding aqueous solutions. The acids as a class illustrate this in a very striking way; for while their aqueous solutions are most excellent electrolytes, their solutions in liquid HCN are only moderately good electrolytes in the case of hydrochloric and sulphuric acid, while the solutions of the organic acids are exceedingly poor conductors of electricity. In the face of these facts, the Nernst-Thomson rule can not be considered as substantiated by the conductivity of solutions in liquid HCN. The authors conclude that the conductivity of a solution is not determined by the dielectric constant of the solvent, its state of polymerization or its spare valences, but rather by the specific nature of the compound formed when solute and solvent act on each other to form the solution. For instance, the relatively high conductivity of amyl amine, strychnine and morphine in liquid HCN is worthy of note; these bases undoubtedly react with the liquid HCN, forming salts that dissolve in an excess of the solvent.

The influence of the solvent in electrolytic conduction has recently been investigated by Patten, the principal results being as follows: The lowering of the specific electric conductivity of non-aqueous solution by the addition of a pure solvent, is approximately proportional to the number of gram-molecules of solvent added; the application of this principle offers a new method of determining molecular weights. The curves of alteration of the specific electric conductivity are peculiar to each solvent; the alteration depends upon the chemical character of the solvent employed, all degrees of this chemical influence of solvent on the original solution, being observed, from water to benzine. The idea is advanced that electrical conductivity is the resultant of, first, the tendency of some molecules to transfer the charge produced by an impressed e. m. f., and, second, the resistance offered to this

transfer of charge by other molecules. Konowalow's conclusion that the small molecular volume of water stands in a definite relation to the power of aqueous solutions to conduct electricity, is unwarranted; also his conclusion that the magnitude of the electrical conductivity of solutions is proportional to the intensity of chemical combination between solvent and solute, as measured by the heat effect. The conduction of electricity by solutions depends upon the fact that a compound is formed by the solvent and solute when solution takes place; and the degree of electrical conductivity depends upon the constituents in this compound, and possibly upon their arrangement. These investigations are described in the *Jour. Phys. Chem.*, November.

The limits of electrolytic conductivity were investigated by BONSFIELD and LOWRY, in a paper in which they point out that, quite apart from the limits due to freezing or boiling, electrolytic conductivity has another lower and an upper limit. At the lower limit the viscosity of the solvent stops the motion of the ions, and at the upper limit the solvent loses its ionizing power. The series of changes may be represented by a curve giving the conductivity as a function of the temperature; this curve has a maximum, depending on the nature of the solvent and solute as well as on the concentration of the solution, the conductivity being a maximum and the temperature co-efficient of the conductivity being zero at this point; as the temperature falls, the conductivity decreases, because the increasing viscosity more than counterbalances the effects of increasing ionization. Over a considerable range the curve follows an approximately linear law, this straight line becoming concave to the horizontal axis at the higher temperatures and convex at the lower temperatures. On this part of the curve the conductivity of the majority of aqueous solutions must be represented, the acids giving values on the concave and the salts on the convex part of the curve. At very low temperature the curve probably becomes asymptotic to the axis of temperature. Above the temperature of maximum conductivity the conductivity also decreases, the decreasing viscosity being now more than counterbalanced by the decreasing ionization of the solution. The decay of ionization becomes more rapid as the temperature rises, and if the solution is not an electrolyte *per se*, the curve runs steadily down and cuts the axis at the critical temperature of the solution. The paper is published in the *Proc. Roy. Soc.*, October 17th, an abstract of which is given in the Lond. *Elec.*, November 28th.

An account of experiments to determine the conductivity of concentrated solutions of sulphuric acid, caustic soda and calcium chloride, which have very low freezing points, is given by KUNZ in the *Comptes Rendus*, November 10th. With a 45 to 70 per cent. solution of sulphuric acid, temperature below—70° could be attained and measured by means of a constantan iron couple. His measurements show that the conductivities of all of these do not converge to zero (that is, infinite resistance) at—39°, as Kohlrausch supposed, but more likely at absolute zero, thus representing the reverse of the case of the pure metals, whose resistivities converge to zero at the same point. An abstract is given in the Lond. *Elec.*, November 28th.

Aluminum Anode.—The curious and somewhat mysterious behavior of aluminum as an anode, in that it stops a current from passing, and may therefore be used as a rectifier of alternating currents, is receiving some much-needed investigation, and the anomalous action is beginning to be more clearly understood. Although much was promised by such rectifiers some years ago, they have not been found practicable with the exception perhaps of the new form described last year by Burgess. Among the recent investigations of this behavior of aluminum is a (Brit.) Physical Society paper by TAYLOR and INGLES, an abstract of which is given in the Lond. *Elec.*, November 28th. They begin by calling attention to the fact that aluminum is very slowly acted upon by dilute sulphuric acid even at moderately high temperatures, which with dilute hydrochloric acid the action is violent, and it is found that if a little hydrochloric acid or a soluble chloride be added to dilute sulphuric acid, the action is as violent as with hydrochloric acid of the same concentration. This peculiar phenomenon is thought to be connected with the other well-known fact that when an aluminum electrode is used as anode in a solution of a sulphate or of sulphuric acid, there is a very great resistance which does not exist when the aluminum plate is cathode or when other acids are substituted for the sulphuric acid; this great resistance is generally supposed to be due to an insulating film. The authors endeavor to explain both phenomena as being due to the same cause. They used a cell containing an aluminum and a platinum electrode in dilute sulphuric acid; they examined the influence of the addition of certain salts; the influence of potassium chloride, bromide, nitrate, acetate, chlorate and thiocyanate were thus investigated and the authors conclude that the presence of certain ions enables a large current to pass through the cell. They think the reason is that the film of aluminum hydroxide on the anode is permeable to certain ions but impermeable to others. The anomalous behavior in sulphuric acid would then be due to the impermeability of the film to the negative sulphuric acid radicle ions and also to the positive three-valent Al ions. This explanation is in agreement with the fact that a reversal of the p. d. acting upon the cell immediately causes a current to pass, the film being permeable to hydrogen ions. They made experiments on the rate of diffusion of various ions through a film of aluminum hydroxide, and found that several salts of potassium diffused rapidly through such a film, but the sulphate passed through very slowly. This strengthens the argument that the abnormal behavior of aluminum anodes in sulphuric acid is due to impermeability. It is suggested that the very small current which does pass may be due to a secondary action at the anode in which the ions of water take part. The theory is confirmed by a series of experiments in which the peculiarities of the aluminum anode are reproduced by means of a platinum anode coated with a film of aluminum hydroxide. A further test was applied in the direct measurement of the resistance of a film of aluminum hydroxide to the passage of different ions. Quantitative experiments which the authors have performed on the effect of the presence of different ions on the reaction between aluminum and sulphuric acid, show that this reaction is accelerated considerably by the addition of potassium chloride.

The theory of a rectifier based on this principle is given in a paper by Guthe, published in the *Phys. Rev.* for December. It has already been abstracted in the ELECTROCHEMICAL INDUSTRY for November.

Depolarization by Potassium Chromate.—MUELLER continues the description, in the *Zeit. f. Electrochemie*, December 11th, of his researches on the effect of soluble chromates in the electrolysis of aqueous solutions of the halogens, represented by a diminution of the reduction at the cathode. This latter influence may be shown by the following experiment: A 1 per cent. solution of potassium hydrate is saturated with potassium iodate and 200 cc. are put into the cell containing platinum electrodes, the anodic and cathodic department being separated from each other by a diaphragm. The current is regulated so that it is just below the point at which there would be development of hydrogen at the cathode; that is, there is perfect depolarization. If, then, 2 cc. of an aqueous solution containing 10 to 20 grams of potassium chromate in 100 cc. are added to the cathodic department, hydrogen begins to develope at the cathode, and at the same time the voltage at the terminals of the cell increases. This is shown to be due to the formation of a diaphragm of an insoluble chromium compound on the cathode. The increase of the voltage at the terminals is due to the fact that before the formation of the diaphragm there existed a strong depolarizer, but after the diaphragm becomes active, the electrolyte behaves as though no depolarizer was present.

Residual Currents.—While it is generally accepted as true

that there is a definite minimum e. m. f. required to decompose a certain electrolyte, yet it is a fact that with any electrolyte, no matter how low the applied e. m. f. is, a current is found to pass; it may be small, but is measurable. This is what was called a "Reststrom" by Helmholtz, who worked with an e. m. f. of 1.1 volt and found that a measurable current passed for weeks at a time through an electrolytic cell with platinum electrodes in distilled water or in dilute sulphuric acid. His explanation is that the solution may originally contain dissolved hydrogen, then this hydrogen present at the anode acts as a depolarizer; at the same time an equivalent amount of hydrogen is liberated at the cathode and will either dissolve in the electrolyte or be occluded; although electrolysis takes place, neither of its products appear and the e. m. f. does not have to do the work implied by the decomposition of water into its components; in other words, a current may pass, although the e. m. f. is less than that required for decomposition; the hydrogen freed at the cathode may diffuse through the liquid until it reaches the anode and so by a constant circulation support the current. If, at the start, the solution or the electrodes contain oxygen instead of hydrogen, the reasoning will be analogous. This view of Helmholtz is supported by the fact that if the gases are artificially removed from the original electrolyte, the "residual current" is much smaller. Bigelow has now made very extended experiments in this same direction, the description of which he published in a long paper in the *Jour. Phys. Chem.* for December. These, he claims, show that Helmholtz's explanation cannot represent the whole truth. His experiments were made with platinum electrodes, and from the results he offers the following new theory: A dissolved gas is assumed to be in a condition analogous to a rarefied gas, some of whose molecules Thomson has shown are capable of carrying positive electric charges, other negative ones. The process of solution is assumed to be sufficient to occasion this differentiation. When a charged gas molecule comes in contact with the metal of the electrode, it gives off its charge; the molecule may then be occluded or remain in solution; in the latter case it increases the concentration of the neutral molecules and thus induces a further differentiation into molecules with opposite charge. If a small external e. m. f. is applied there will be a tendency for one electrode to attract positively charged molecules, and for the other to attract negatively charged molecules. Though the charge on the individual molecule is probably the same as that on the ion, the former are present in such small numbers that the total current carried by them is much less than that carried by the ions when the decomposition point is once passed, in fact negligible in all ordinary work. This theory enables one to say that there is a real and definite decomposition point for each pair of ions under given conditions; any current observed before this value is reached, being due to the charged molecules present. Unfortunately he used platinum plates, which have the property of combining with oxygen and hydrogen, and this necessarily limits his conclusions to such plates. Not until a material is used which is absolutely passive, can general conclusions be drawn.

Formation of Ozone.—Warburg has recently investigated the production of ozone by discharges in a closed volume of oxygen. In this case the formation of ozone has a limit which varies with the conditions of the experiment. Besides the ozonizing effect there exists a contrary effect which counterbalances it after a time. Since for the limited duration of the ozonizing process the spontaneous decomposition of the ozone is negligible, it follows that the electric discharge itself must produce the contrary effect. In endeavoring to obtain a measure of both effects, he starts from the assumption that the ozonizing effect is proportional to the number of molecules of oxygen present, while the decomposition is proportional to the number of molecules of ozone present. There is a decided difference between the behavior of a positive discharge and that of a negative discharge; the maximum percentage of ozone is about three times as high for negative as it is for positive discharges. If, after the negative maximum is reached, the mixture is subjected to the positive effluvium, the percentage falls to the positive maximum. The decomposing activity is the same for positive and negative electricity, but the ozonizing action itself is three times higher for negative electricity. The effect of temperature on both discharges is the same. The results are given in the *Ann. d. Phys.*, November 12th, and abstracted in Lond. *Elec.*, December 19th.

Electrolytic Oxidation of Organic Substances.—An account of experiments on the electrolysis of formic acid and oxalic acid, also of potassium carborate, is given by Salzer in the *Zeit. f. Elektrochemie*, December 4th. His investigation is only preliminary, but shows the great difference in the reaction and especially in the anodic potential difference, when a bright platinum, as distinguished from a platinized platinum anode, is used.

Crystallization from an Electrolyte.—Heyl gives an account of an experimental investigation of this subject in the *Phys. Rev.* for December, in which after failing to find any effect produced by electrostatic stress upon the formation of crystals, he studied the effect produced on an electrolyte carrying a current, but again obtained negative results. Two substances were used, one was copper sulphate in an aqueous solution, and the other mercuric iodide in concentrated hot hydrochloric acid. The passage of the current produces no effect comparable with that produced by the heating of the solution.

Alloys of Lead, Tin and Bismuth.—A very long experimental investigation of the alloys of lead, tin and bismuth from the standpoint of the principles of physical chemistry, especially the phase rule, has recently been made by Shepherd. From alloys containing lead, bismuth and tin, he found that the pure tin crystallizes, but often in an unstable, denser form, and that lead and bismuth form two series of solid solutions, in each case with contraction. When the fused alloys are cooled fairly rapidly, the saturation concentrations are not reached. His researches are published in the *Jour. Phys. Chem.*, November.

Electric Origin of Molecular Attraction.—An attempt to reduce molecular action to the electron theory, has recently been made by Sutherland, in a paper in the *Phil. Mag.* for December. He starts with the conception of a neutral gaseous molecule, containing positive and a negative electron, and shows that there is a strong contrast with the law of gravitation; the first condition of the electron theory is satisfied by the fact that molecular mass does not enter into the expression for molecular attraction. It may be considered that the two electrons of a molecule like NaCl, when giving the line spectrum of sodium, revolve round one another in a circle of such size that centrifugal force and electric attraction are in equilibrium; perhaps they revolve entirely within the Na atom. An abstract may be seen in the Lond. *Elec.*, December 12th.

Laboratory for Electrolytic Analysis.—The first part of an illustrated description of the laboratory for electrolytic analysis of the Electrochemical Institute of Nancy, is given by Richard in *l'Eclairage Elec.*, December 13th.

PRIMARY AND SECONDARY BATTERIES.

Storage Batteries.—The general problem of the storage battery, involving its possibilities and its future, has been the subject of numerous articles during recent years, and while there is a general similarity between them, and while the results of such opinions do not seem to have had any very beneficial effect, other, perhaps, than to discourage the investigation of radically new types, yet the views of recognized authorities are nevertheless of interest, even though the prophecies of experts do not always come true. Stated briefly, the opinions seem to exist that no other type of storage battery will be found than the present lead battery, and that this lead battery is not what is desired. To predict that nothing new will ever be found in a field where there is a possibility of an

infinite number of combinations of an almost infinite number of chemical materials, seems presumptive; and may not the general condemnation of the much abused lead battery be due largely to the fact that we expect more from it than is possible to obtain in practice? Many of the faults found with the lead battery may equally well be applied similarly to human beings; our life is limited and we resent abuse; yet we would not like to admit that we are complete failures.

The latest comments on the storage battery problem are by SWINBURNE, who, in his presidential address to the (Brit.) *Inst. Elec. Eng.*, discusses the problem of their design as follows: He believes that we are practically limited to lead, at any rate in acid cells. The plate which is anode during discharge should not dissolve in the electrolyte, for if it does the deposition and solution will be uneven, and the plate will grow trees and comes to grief. This excludes zinc and iron unless a suitable electrolyte is found. On the other plate an insoluble depolarizer is needed, or else a double fluid cell must be used, involving a porous diaphragm, diffusion and impracticability. Not only must the depolarizer be insoluble, but it must be converted into an insoluble body on discharge. The coating must be a conductor in one state or the other, or there will be no proper contact. In the lead cell there is always enough peroxide and metallic lead in the coating to secure electrical contact though the discharge product is an insulator. The depolarizing coating must be connected to a conducting plate which is not attacked by local action. Lead and silver are the only available metals, and sulphuric and perhaps phosphoric, the only acids, for the nitrate of lead is soluble and hydrochloric acid is decomposed by lead peroxide. Lead is protected by its coating of sulphate or peroxide, as the case may be. "It thus seems as if we were limited almost absolutely to lead and sulphuric acid. It is wonderful that we have the lead cell at all. We owe it to the chance observation of Planté. The theory was not understood for a long time. For many years it was thought that the pressure was due to the PbO_2 and Pb, changing into Pb O. The acid was merely put in to make the electrolyte conduct, and sulphuric was used because people used it in gas voltmeters, and they never thought that it ought to be as strong as practicable to give the pressure and output. The difficulty of lead sulphate was regarded as a difficulty to overcome." What is wanted in the lead cell, is lightness, large capacity, cheapness, rapid discharge, efficiency and mechanical strength and durability, but these qualities are mostly antagonistic; large capacity means rapid deterioration, mechanical strength means weight; there is, therefore, no use in testing a cell for capacity without testing the efficiency and durability too; published battery reports are often misleading, because they omit essential information. In alkaline cells, although the e. m. f. is smaller, the metals admit of light plates and grids, and the coating may conduct in both states, instead of in only one as in lead cells, so that a larger proportion of the coating may be active. "The future of this type of cell is uncertain, as very little has been published as to results." This part of his address will be found reprinted in the Lond. *Elec.*, December 19th.

Dry Cells.—ZACHARIAS, who has written on similar subjects before, believes that the manufacture of dry cells has passed through a state of rapid development in the last two years, especially in the production of very-small cells which are very useful for pocket lamps for physicians, travelers, for use in the army, etc. In the ordinary dry cell he claims that not one-quarter of the depolarizer is consumed under ordinary circumstances, while in cells of small dimensions the efficiency is better. In general, cells of two sizes are made, the larger one is 70 mm. high and has a cross section of 35 mm. in square; the smaller one is 55 mm. high and has a diameter of 20 mm. Three such cells, sufficiently insulated from each other, are generally put together and surrounded by a card-board cover. The small incandescent lamps are generally provided with a reflector and a lens, and consume 0.25 to 0.3 ampère at 3.5 to 4.0 volts. One cell of the smaller size has driven an electric clock for four weeks, the current being 7 milliamperes. The author urges that in installing electric bells, etc., in houses, the proper dimensions of the wires should be chosen; that is generally not done in practice and much power of the dry cells is wasted. The carbon rods of the small cells are about 6 to 7 mm. thick and the surrounding depolarizing mass has a diameter of 14 to 16 mm.; it is held in position by four small glass tubes, for the sake of proper insulation from the zinc electrode. The distance between depolarizer and zinc electrode is only 1.5 to 2 mm. The electrolyte is to be filled into the space between the zinc and the depolarizer in a thick but easily flowing form, and is afterward made less liquid by special means. Even the best of these small cells, when continually used to light a lamp, last only fifteen minutes, they should therefore be used only momentarily, but notwithstanding this they are very useful for various purposes. His article is in the *Centralbl. f. Accum.*, December 1st and 15th, where he also gives some notes on testing such small dry cells.

MISCELLANEOUS.

Capillary Electrometer.—In many electrochemical researches the voltages to be measured are very low, of the order of one volt or less, and for such low voltages the usual forms of voltmeters are not, as a rule, satisfactory. Moreover they require quite a perceptible current, which is the very thing that one wants to avoid in any electrochemical measurements. The capillary electrometer, therefore, is of special interest for such researches, as it takes no current at all, and its total range is within about one volt.

The following description of a new form by BURCH, abstracted from his Royal Society paper, reprinted in the Lond. *Elec.*, December 19th, will therefore be of interest. Fig.

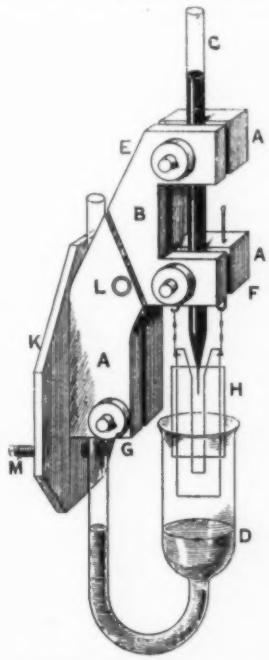


FIG. 1—CAPILLARY ELECTROMETER.

1 shows the instrument in its final form and Fig. 2 shows the details of the capillary through which is the essential part. The support A is cut from a solid block of ebonite 9 cm. long, 5 cm. wide, and 2 cm. thick; the capillary tube is C. Adjustments for setting the capillary tube at right angles to the optic axis and parallel to the slit of the photographic recording apparatus, are provided for by the stout brass plate K; the screw, M, fastens it to the adjustable stand of the pro-

jection microscope.' The brass plate K is so shaped that there is a space of about 3 mm. between it and the left-hand side of the ebonite support A, in order to leave room for the adjustment of the latter about L as a center. The construction of the capillary trough is shown in the diagrams, Fig.

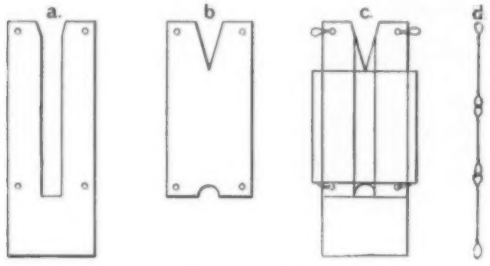


FIG. 2—CAPILLARY ELECTROMETER.

2, *a*, *b*, *c*. A piece of mica, such as is used for lamp shades, is cut to the shape *a* with a pair of scissors; four holes are drilled with a needle in the positions shown, and a thin piece of the best clear mica is then selected, the piece *a* placed on it, and four corresponding holes pricked through with the needle, the piece being afterwards cut to the shape *b*. Finally, *a* and *b* are fastened together by four little loops of No. 30 platinum wire, and the whole trimmed to shape with the scissors. The trough is then hung by two platinum chains; these are made of No. 30 wire, with long links, as shown at *d*, Fig. 2, so that the acid may not creep up them; they are hung from the hooks shown in Fig. 1, which are best made of half-round wire, doubled like a linch-pin, sliding easily but firmly in holes on each side of the capillary tube, as shown in Fig. 1. The operation of putting in a capillary is as follows: The instrument is fixed to any convenient support by the screw M; the milled head G is loosened, and the U-tube drawn down and turned aside; the whole instrument is then tilted backwards to an angle of 45° from the vertical; in this position the trough H hangs clear of the capillary tube; if the capillary tube has already been filled and connected with the pressure tube, the nuts E and F must be unscrewed far enough for the tubes to pass sideways into the clamps, but a new capillary may be easily and safely inserted from below after merely loosening E and F. It must then be filled to within 2 cm. of the top, but not nearer, with recently distilled mercury from a perfectly clean pipette; it is then connected with the pressure apparatus, and some mercury forced through. The screw M is then slightly loosened, and the instrument raised cautiously to a nearly vertical position. The trough H is adjusted by sliding the hooks up or down, or bending them until the capillary rests against the center of it, the apparatus being tilted back during each alteration. When these adjustments have been made, the inside of the trough is wetted by touching it with a glass rod dipped in dilute sulphuric acid of 25 per cent., and the apparatus is tilted forwards until the wet trough swings against the capillary and sticks to it. A piece of thin cover glass, or mica, if very high powers are to be used, slightly wider than the trough, wetted on one side with the acid, and placed carefully against the trough, to which it adheres, holding it firmly against the capillary, the lower edge of the glass resting against the platinum loops with which the trough is fastened together, as shown in Fig. 2, *c*. The U-tube is then turned back into position, cautiously raised until the lower edge of the glass just dips into the acid, and clamped by the screw G. Finally the trough is gently shaken or pushed to and fro in the plane of the mica, until the acid rises in it to the required height and all the bubbles are expelled. The definition, with these electrometers, is perfect. The capillary touches the cover-glass throughout its length, so that any dry objective can be used. The microscope should not, however, be left focussed on the capillary, lest the acid should by chance get between the objective and the cover-glass.—Lond. *Elec.*, December 19th.

Sewage Purification.—An account of experiments made at Salford with various processes of purifying sewage electrically, by Corbett, is given in Lond. *Engineering*, December 26th. The requirements at Salford are governed by the fact that the sewage to be treated is that of a manufacturing town of nearly 250,000 inhabitants, where trade wastes in great variety are admitted to the sewers, and where a large quantity of mere land water enters the sewers also. Among the processes tried was Webster's electrolytic process, and it is said to have been in many points the most unique and most successful of the processes experimented with. Its cost was somewhat high, though by no means the highest considered practicable, and it would have been adopted for the Salford sewage works but for the inability of the company promoting it to finance so large a scheme. In this process no chemical precipitants are used, but "the sewage is passed between cast-iron plates, alternately connected with the positive and negative wires of a dynamo. The effect of this is much like that of chemical precipitants, the sewage being separated into clear liquid and flocculent particles, which subside into sewage sludge in ordinary precipitation tanks." The tank effluent is clear and non-putrescible, but contains fine particles of sesquioxide of iron which give it a rust tint, and this can be readily removed by rapid filtration through a fine sand and gravel filter, the result being a perfectly bright and almost pure filtrate. About half the cost of working is for power to produce the electricity required; this process might therefore be cheap in a place where water-power is available. The company's offer was to treat the Salford sewage for twenty years at $15.06 per million gallons, they providing all the plant, etc., and the plant to be transferred at a valuation at the end of the term. In an appendix the following figures are given concerning this process. The requirements per million gallons of sewage treated per day were as follows: steam engines of 41.76 indicated horse-power; electric horse-power therefrom 33.4; average voltage employed, 41.02; iron used from the electrodes, 428 pounds (this equals about 3.2 grain of iron per gallon).

Niagara Falls.—Illustrated articles on the new plant of the Canadian-Niagara Falls Co. are given by Dunlap in the *Sc. Am.*, December 6th, and *Eng. News*, December 11th.

ANALYSIS OF CURRENT ELECTROCHEMICAL PATENTS.

By George P. Scholl.

ELECTRIC FURNACES AND FURNACE PRODUCTS.

Electric Furnace. A. A. Shade, Chicago, Ill. Patent No. 713,923, November 18, 1902. Application filed December 28, 1901.

The specification describes an electric furnace intended for smelting or reducing ores and other fusible substances. It belongs to the type of electric arc furnaces, and the vertical cross section given in Fig. 1 shows three arcs arranged one above another, D_1D_1, D_2D_2 and D_3D_3. The shaft of the furnace is constructed in a peculiar manner, with projecting ledges and corresponding recesses below the electrodes, for the purpose of retarding the fall of the material and exposing it more thoroughly to the heat of the arcs, which are deflected towards the ledges by means of magnets E_1E_1. Another magnet E_2 is arranged

below the crucible C, so as to deflect the arc between D_4, D_5 into the crucible. The material is fed into the furnace through hopper J_2 and pipe B, and while passing through the conveyer it is dried in the chamber K, which is heated by the waste gases of the furnace, entering through pipe K_1. The body of the furnace is surrounded by a metallic casing A_2, held together by iron bands A_3, and the space between the body of the furnace and the casing is filled with insulating material A_4, as mineral wool, asbestos, etc. The electrodes are insulated from the casing by insulating rings A^2, and are supported in a sliding yoke G. They can be moved forward by means of hand wheel G_2 and spindle G_1, which bears against a cap fitted to the end of the electrodes. Shields F are provided below the magnets in order to confine the action of the magnets to the arc above them, and to prevent them from influencing the arc below. The crucible C is arranged so that it can be withdrawn from the furnace if necessary. A^5, A^6 are peep holes between the electrodes and on a level with the respective ledges. A^1, A^4 are passages in the walls of the furnace,

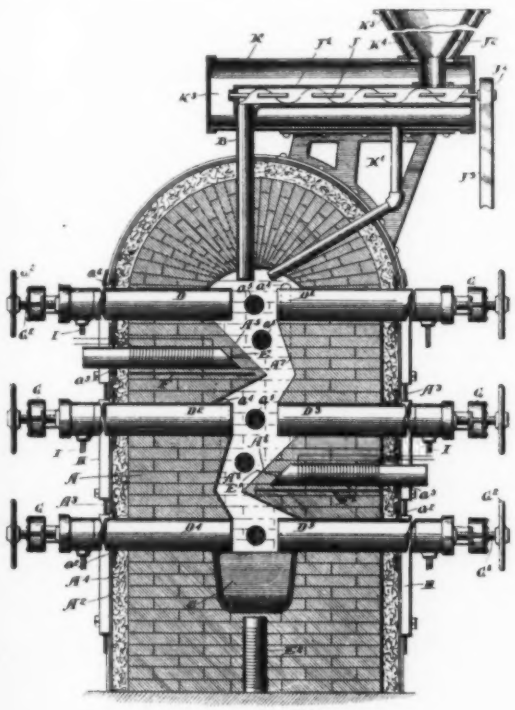


FIG. 1—SHAPE ELECTRIC FURNACE.

intended to permit the furnace gases to pass upwards through the furnace without being required to pass through the arcs.

Electric Dental Furnace. A. M. Hewett and J. C. Smith, Chicago, Ill. Patent No. 714,373, November 25, 1902. Application filed February 17, 1902.

The furnace is a portable one, constructed of an outer and inner muffle of fire clay. The inner muffle is provided with a screw thread on the outside, for the purpose of providing a seat for the heating coil.

Electric Furnace. H. N. Potter, New Rochelle, N. Y. Patent No. 715,505, December 9, 1902. Application filed November 21, 1901.

This furnace is an improvement on the inventor's former patent, No. 652,640, of June 26, 1900, in which the main source of heat was an electrolytic tube composed of a mixture of dry electrolytes and supplied with terminals for conveying electric current to the tube, which is kept in a state of incandescence by the current after a preliminary heating by external means. The present invention relates to providing means for preventing the current in such a tube from flowing unevenly, by reason of almost unavoidable slight differences in specific resistance of the tube, due to structural, and perhaps chemical, irregularities in the tube material. These difficulties are overcome by notching the tube, or building it up of alternate sections of relatively good and relatively poor conductors, or by imbedding rods of the good conducting material in a jacket of poorer conducting material. The mixture of dry electrolytes referred to above is a mixture of magnesia and alumina, and as poorer conductors, pure magnesia or pure alumina are proposed. The unmixed electrolytes being poorer conductors than the mixtures, the current will pass along the better conducting segments.

Electric Furnace. H. N. Potter. Patent No. 715,506, December 9, 1902. Application filed November 21, 1901.

The furnace consists essentially of a single carbon tube, lined with magnesia and coated with the same substance, surrounded again by a jacket of calcium oxide, the whole being then inclosed in a larger tube of glazed stoneware. The specification deals mainly with the mechanical means adopted to meet the problem of the expansion and contraction of the parts of the tube, which are alternately heated and cooled, and for which provision has to be made, on account of the intense heat at which the furnace is to be run. Moreover, as the material proposed for the jacket—namely, calcium oxide—is a hygroscopic substance, subject to slacking, means have to be provided to protect it, which is done by arranging a stuffing ring at or near the air inlet, in such a position that it will absorb moisture from the indrawn air and can be itself rapidly removed if necessary. Other materials of a heat-insulating and refractory nature, such as chalk, asbestos, etc., can be substituted for calcium oxide in the jacket.

Tubular Electric Furnace. H. N. Potter, New Rochelle, N. Y. Patent No. 715,507, December 9, 1902. Application filed February 7, 1902.

The same inventor declares in this specification that a carbon tube furnace is subject to sagging or warping out of shape under the influence of extreme heat, the carbon becoming plastic at the high temperature reached in the furnace, while other substances, such as magnesia, which are also used to form the body of such furnaces, are still more subject to distortion of shape under the influence of heat. The means proposed to overcome this difficulty consist in a series of carbon collars surrounding and supporting the internal tube throughout its length, the collars extending from the tube at right angles into a region which is much colder than that next to the tube. The construction does not interfere with the use of a jacket, as described above, as the carbon collars extend into or through the jacket. The whole structure, including the jacket and the collars, is then inclosed in a jacket of non-conducting material, *f. i.*, glazed stoneware, as referred to above.

Electric Furnace. H. N. Potter, New Rochelle, N. Y. Patent No. 715,508, December 9, 1902. Application filed March 27, 1902.

The inventor says: "In an application filed by me on November 21, 1901, I show and describe a lined carbon furnace tube, in which the tube rotates about its axis in order that the melted lining material may flow evenly over the inner surface of the carbon tube, while that invention also contemplates the rotation of the furnace tube for other purposes, as when metallic chromium is produced by a continuous operation and the material is worked steadily through the furnace, partly by the effects of the rotation of the tube. The present invention contemplates making the furnace of a double tube." Provision is therefore made to have the main carbon tube stationary and to arrange inside of it a comparatively thin-walled tube, which is to be revolved. By this means it is possible to renew the inner tube very easily. Connections to the main tube are much less complicated than if it rotated, and the space between the two tubes can be filled with an inert gas. The

inner tube may either be of carbon or of a material such as magnesia, zirconia, or the like. For operations such as tempering steel, firing enamel and making alloys, the advantages of having an inner rotating carbon tube can be secured without the use of the latter by merely having a rotating magnesia lining, the temperature not being sufficiently high to cause the lining to adhere to the carbon furnace walls.

End Support and Circuit Terminal for Carbon Tube Furnace. H. N. Potter, New Rochelle, N. Y. Patent No. 715,509. Application filed March 28, 1902.

This patent describes improved means for making electrical terminal connections with carbon tube furnaces, and for mounting such furnaces in such a manner as to permit expansion and at the same time provide good mechanical support. The means employed for this purpose are metallic diaphragms at each end of the carbon tube; these diaphragms serving also as parts of the electrical connections at the ends of the furnace tube.

Process of Obtaining Metallic Aluminium or Other Metals by Electrolysis. Girolamo Taddei, Turin, Italy. Patent No. 715,625, December 9, 1902. Application filed July 17, 1901.

This invention relates to a process for obtaining metals from their compounds, and particularly the metal aluminium from its oxide, and the object is to effect this with the minimum of energy thermoelectrically considered in relation to industrial conditions, and to effect it in an automatic, or substantially automatic, and continuous sequence of steps or operations. Fused sodium chloride is first decomposed by electrolysis, and its elements are obtained in the form of vapors, the temperature being about 1,000° C. and the voltage about 4.5. The chlorine vapors are then introduced into a vessel charged with balls formed from a mixture of tar and dehydrated alumina, in which the proportions of the ingredients are as 6 of carbon to 9.1 aluminium. This vessel and its contents are heated up to from 1,300° to 1,500° C., and the chlorine, as it is gradually brought in contact with all parts of the mass, produces a reaction, resulting in the formation of aluminium chloride and carbonic oxide, according to the equation $Al_2O_3 + 3C + 6Cl = 2AlCl_3 + 3CO$. The aluminium chloride from this reaction, being in the state of vapor, passes, together with the carbonic oxide, into another vessel, where it comes into contact with the sodium vapor generated by the electrolysis of sodium chloride in the first step of the operation. Here another reaction takes place; the sodium combines with the chlorine of the aluminium chloride and sets free the metallic

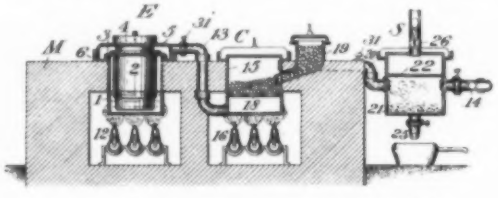


FIG. 2—SECTION OF ALUMINIUM APPARATUS.

aluminium, $2AlCl_3 + 6Na + 3CO = 6NaCl + 2Al + 3CO$. Thus, says the inventor, the metal aluminium is separated, the sodium chloride is recovered without loss for use again and the carbonic oxide passes off and may be burned. The operations are continuous, the mixture of alumina and tar producing continuously aluminium and carbonic oxide. The sodium and chlorine, separately and in combination, move in a closed circuit without waste or being consumed. The accompanying Fig. 2 gives a longitudinal vertical section of the apparatus in which the process is to be carried out, and Fig. 3 represents the plan. The whole apparatus is set in masonry M, and is divided into three sections, the electrolysis taking place in E, the chlorination in C and the substitution in J. Section E consists of a vessel 1, into which depend separator tubes 2, fixed at their upper ends in an inner cover 3. The carbon anodes 4 depend in these tubes from an upper or outer cover 5, above the cover 3. The edges of the covers rest in a trough 6 around the vessel 1. At the side of the vessel 1, and connecting with it by apertures 7, is a vessel 9 for introducing the electrolyte or making additions during the process. The cathodes are of iron, and situated between the anodes; they are not indicated in the figures. From the space between the covers 3 and 5 two pipes 13 lead to the chlorinating section C, and pipe 14 leads from the interior of vessel 1 to the substituting section S. Section C consists of a vessel 15, divided into two chambers by a transverse partition, each chamber having a false perforated bottom, below which the chlorine enters. Raw material is introduced through hoppers 19, and pipes 20 lead to

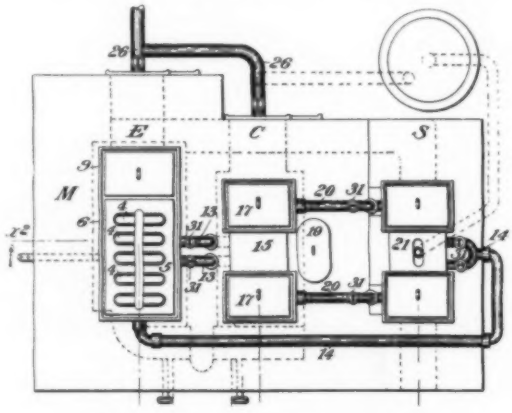


FIG. 3—PLAN OF ALUMINIUM APPARATUS.

section 5. This section comprises a vessel 21, divided transversely by a partition 22 into two chambers, with covers 23. In each chamber there is also a horizontal partition 24, which extends from partition 22 part way across the chamber. Pipes 20, from vessel 15, and forked pipe 14, from vessel 1, enter below the partition 24. A pipe 26, with forked connection to the chambers in vessel 21, carries off the gases (CO) to the burners 12 and 16. The process is carried out by electrolyzing sodium chloride in vessel 1, the chlorine passing out between the covers 3 and 5 and through pipes 13 into vessel 15. There it acts on the mixture of alumina and tar, and the aluminium chloride and carbonic oxide produced in the reaction pass through pipes 20 into vessel 21, where they meet the sodium vapors conveyed from vessel 1 by pipe 14. Reaction takes place, metallic aluminium and sodium chloride being precipitated, and carbon monoxide escapes through pipe 26 and is led underneath the vessels 1 and 15, where it is burned. In order to separate the aluminium from the sodium chloride, it is proposed to put the mixture into the vessel 9 of section E, where the sodium chloride melts and replenishes the electrolyte, while the aluminium falls to the bottom and may be drawn off. The above process has been outlined at such length on account of the importance which would attach to any new method by which the cost of production of aluminium could be reduced. When it is compared, however, with the simple methods which are in use at present, it does not appear as though such an involved process, with its complicated apparatus, would be likely to accomplish a reduction in the cost of production.

Apparatus for Obtaining Metals by Electrolysis. G. Taddei, Turin, Italy. Patent No. 715,626, December 9, 1902. Application filed December 13, 1901.

This patent covers the apparatus used for carrying out the process described above. The wording of the specification is almost exactly the same as that of the preceding one, and nothing new is disclosed as to the nature of the material of which the apparatus is constructed. Anybody who has ever attempted to electrolyze sodium chloride, even at much lower

temperatures than are given by the inventor, knows how quickly metallic, as well as clay and porcelain, vessels are destroyed if they are heated from the outside. Furthermore, it is also well known that the higher the temperature of the electrolyte, the worse the yield of sodium (Borchers, "Electrometallurgie," p. 60).

Carbophosphide of Calcium. C. S. Bradley, Avon, N. Y., and R. H. Read and C. B. Jacobs, East Orange, N. J., assignors to the Ampère Electrochemical Co. Patent No. 716,812, December 16, 1902. Application filed April 20, 1898.

The new product described is obtained by heating a mixture of definite proportions of normal calcium phosphate, burnt lime or limestone and carbon in an electric furnace. The ingredients should be well mixed, and, with a mixture of two molecular

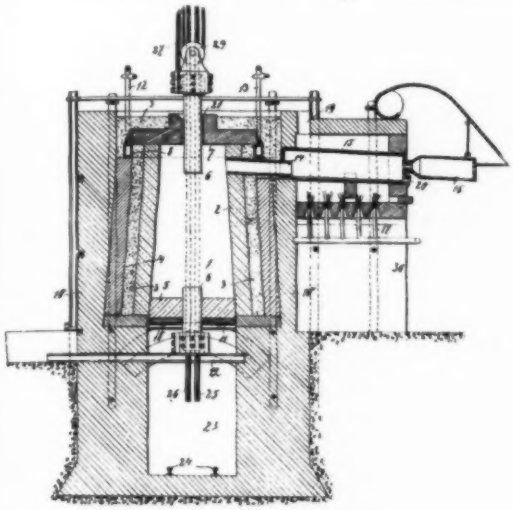


FIG. 4—DORSEMAGEN FURNACE.

equivalents of burnt lime, one of normal calcium phosphate and sixteen of carbon, reaction is stated to take place at the high temperature of the electric furnace, according to the equation $2CaO + Ca_3(PO_4)_2 + 16C = Ca_3C_2P_2 + 10CO$. The material is obtained in a stable, fused mass, which may be tapped from the furnace and allowed to cool, and is described as a homogeneous mixture of carbide and phosphide of calcium, the union of the two materials being analogous to that in the case where two or more metals unite to form a homogeneous alloy. The material, when treated with water, decomposes, yielding a gas which contains acetylene, gaseous phosphide of hydrogen (PH_3) and liquid phosphide of hydrogen (P_2H_4) or its vapor. The presence of the last body renders the whole mixture spontaneously inflammable, so that if it is thrown into water or brought in contact with a wet surface gases are generated at once and burst into flame. The product is stated to be useful as a weapon of war. For instance, in naval warfare, when it can be projected into the vicinity of the enemy, and on coming in contact with the water a large amount of inflammable gases will be generated, which will at once ignite and force the enemy to retreat.

Working Zinc and Substances Containing Silicic Acid in Electric Furnaces. Alfred Dorsemagen, Wesel, Germany. Patent No. 716,008, December 16, 1902. Application filed August 24, 1901.

The inventor of this process has conceived the idea of uniting the production of carbide of silicon (carborundum) with that of metallic zinc by subjecting either naturally-occurring siliceous zinc ores, as willemite, or artificial mixtures of roasted zinc ores and arenaceous quartz, mixed in suitable proportions with anthracite coal, to the heat of the electric furnace. In accordance with the equation $Zn_2SiO_4 + 5C = Zn_2 + SiC + 5Co$, carborundum is produced, and metallic zinc vapors given off. The operation is carried out in the furnace illustrated in Fig. 4, where 1 designates the furnace shaft, with side walls 2 and bottom 5 of carbon bricks. A layer of very fine sea sand 4 is rammed between the carbon lining 2 and the fire-brick work 4; 6, 6 are the carbon electrodes, between which a core of coke is rammed when the furnace is charged with the ore and coal mixture; 14 in an outlet tube for the zinc vapors; 15 and 16 are condensing chambers for the zinc vapors; 23 denotes a chamber in the bottom of the furnace, intended to accommodate a car, into which the material discharged from the furnace can be received. The process looks as though it was a very expensive one, as far as zinc is concerned, but perhaps the latter is only to be considered as a secondary product, the main product being carborundum. It does not look as though the inventor intended to separate the crystalline from the amorphous carborundum, as Mr. Acheson does, for the furnace does not look as if it was designed to be dismantled after each operation.

Tap-Hole Plug. Andrew Dickey, Buffalo, N. Y. Patent No. 714,150, November 25, 1902. Application filed December 2, 1901.

The specification describes a tap-hole plug, especially designed for closing the tapping hole in pots for the reduction of aluminium, where metallic or clay plugs cannot be used, owing to the contamination of the aluminium by the metal of the plug or the silicon of the clay. The plug consists of wood sawdust or paper pulp, either compressed with a suitable binder, like paste or size, or of paper wrapped in layers, the object being to produce a plug of carbonaceous material, such as cellulose, which will, when heated, be converted into a porous, friable charcoal, and which can easily be removed, if desired, without necessitating the use of drilling tools, etc., thus avoiding the danger of injuring the carbon lining of the melting pot. The green plug is placed in the tapping hole, and is converted into charcoal at its inner end by the molten material, but, on account of the low heat conductivity of the material, the carbonization only spreads very slowly to the other parts of the plug.

APPARATUS AND PROCESSES FOR THE ELECTROLYTIC PRODUCTION OF METALS AND COMPOUNDS.

Process for Precipitating Metals from Solutions Containing Same. T. Muffly, Bowdre, Ga. Patent No. 714,599, November 25, 1902. Application filed January 22, 1902.

The object is to provide an improved process for precipitating metals from solutions of alkaline cyanides, bromides, chlorides and hyposulphites or, more particularly speaking, for precipitating gold and silver from solutions of cyanide of potassium, by which said metals have been dissolved out of ores and the like. The novelty of the invention consists in the construction of the electrolytic vessel and of the cathode. The vessel shown in Fig. 5 is divided into two unequal compartments *a* and *b* by a partition *c*. In the compartment *b*, and right against the partition, is placed the anode *e*, of iron, platinum, etc. The cathode *f* consists of a cellular porous carbon plate *g*, placed between two cellular porous carbon casings *h* and h^2, composed of carbon derived from the destructive distillation of tar, resin, oil etc. Between them is placed a packing *i* of filiform lead and zinc composition, consisting of an alloy of 20 parts of lead to 80 parts of zinc. The carbon plate *g*, casing *h* and h^2 and filiform packing *i* are inclosed in a cover g^2 of cotton cloth. Between the anode *e* and the

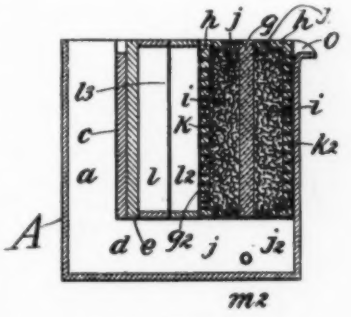


FIG. 5—GOLD DEPOSITION TANK.

cathode *f* is a space inclosed by frames *l* and l_2, of glass, porcelain or other non-conductor, and between these frames is preferably placed a screen f^2. Five such boxes are arranged, each having an independent battery of its own, and the electrolyte flows from one to the other. A perforated pipe is arranged under the cathode, by which either hot or cold air is blown into the apparatus. After the electrolysis is finished, the carbon plate *g* and carbon casings *h* and h^2 are incinerated, the ashes containing the gold and silver are added to the product of the filiform packing *i* and the product smelted into bullion. The purpose of the glass or porcelain frames *l* and l_2 is explained by the inventor as follows "In limiting the electrolytic field between the electrodes *e* and *f* in one compartment *b*, with independent electrical connections with the battery, I secure a more perfect polarization of the solutions. By confining the electrolytic field within the insulating frames *l* and l^2, with the fabric filter screen between them, I prevent floating non-metallic precipitates at the anode *e* from passing through and corroding the cathode *f*, which results in a purer gold and silver product and more effective chemical action. In this method as a whole I secure a perfect and constant polarization of the compound molecules of the solution and a more rapid and complete deposition of the gold and silver atoms at the cathode."

Apparatus for Separating Metals from Solutions Containing Same. T. Muffly, Bowdre, Ga. Patent No. 714,598, November 25, 1902. Application filed January 22, 1902.

This specification is nearly identical with the preceding, and claims specifically the apparatus described above.

Process of Electrolytic Separation of Copper and Nickel. David H. Browne, Cleveland, Ohio. Patent No. 714,851, December 2, 1902. Application filed January 27, 1899. Renewed September 19, 1902.

The process consists in the electrolysis of a solution of cuprous and nickel chlorides. This is prepared by placing copper-nickel fragments into a long, narrow receptacle and simultaneously subjecting it to the action of a solvent for cuprous chloride, such as salt water, introduced into the top of the aforesaid receptacle, and a stream of chlorine introduced at the side of the receptacle. The chlorine is the product of a later operation. The combined action of the salt water and of the heat produced by the combination of the chlorine with the copper-nickel alloy are said to form a solution of cuprous and nickel chloride, which is run into an electrolytic cell. Here it is electrolyzed between copper-nickel anodes and (presumably copper) cathodes. The cuprous chloride is said to be decomposed, the chlorine combining with the copper-nickel alloy of the anode to form cuprous chloride and nickel chloride again. In this manner all the copper is "plated out," and only nickel chloride remains, which is drawn off and freed from iron and traces of copper by precipitation with caustic alkali. The liquor is then heated to a temperature of between 30° and 60° C., concentrated to 30° to 50° Bé, and electrolyzed in a cell with a nickel cathode and a carbon anode, placed in a porous diaphragm. The chlorine given off here is utilized, as mentioned above, for obtaining fresh electrolyte.

Anode. F. McDonald, Johnsonburg, Pa. Patent No. 715,684, December 9, 1902. Application filed April 7, 1902.

The invention relates to anodes for electrolytic apparatus designed for the electrolysis of metallic salts, the object being to provide an anode simple of construction and advantageous in widely diffusing the current without undue heating. The anode consists of a tube of glass, or other suitable insulating material, filled with mercury, into which the positive wire is introduced at the top. A number of platinum strips are fused into the lower part of the tube, and it is stated that, in a vessel about 5 feet long, 12 inches wide and 12 inches deep, these strips will be preferably 10 inches long and 2 inches wide. This anode seems to be somewhat expensive for the electrolysis of metallic salts.

Electrolytic Apparatus. Joseph Matthews, Kings Heath and William Davies, Selby Park, England. Patent No. 715,281, December 9, 1902. Application filed March 29, 1901.

The apparatus is designed for stripping tin from scrap-tinned metal and depositing it on the cathode. It consists of an outer metallic tank, which at the same time serves as cathode and an inner circular-bottomed tank, insulated from the outer tank. The bottom and sides of the inner tank are formed of perforated insulating material, and the scrap metal, which is introduced in the inner tank and forms the anode, is constantly agitated by the radiating arms of a revolving drum, located in the inner tank. The electrolyte consists of caustic potash and protochloride of tin, heated to a little under the boiling point. Provision is also made for using independent cathodes.

STORAGE BATTERIES.

Storage Battery. S. Laszczynski, Berlin, Germany. Patent No. 714,201, November 25, 1902. Application filed February 23, 1901.

This invention is stated to be an improvement in the construction of zinc-alkali storage batteries. A frame or grate, or any suitable form of electrodes, is pasted with zinc sponge, zinc oxide or zinc combinations in the same manner as with lead-sponge plates. Instead of employing zinc plates for the carrier frame, it may be made of amalgamated iron or nickel plate, or other suitable plate. A number of electrodes thus formed are mounted to alternate with nickel oxide plates, being separated from the latter by a piece of parchment only, the electrode block thus formed being then placed in a receptacle exactly large enough to contain it. As electrolyte, a solution of potassium or sodium aluminates, in which the zinc oxide is insoluble, should be used. Since the electrodes lie very close together, there will be room for comparatively little liquid. As invention is claimed: a storage battery having a negative electrode of nickel oxide, a sponge-zinc plate as positive electrode and as electrolyte a solution of potassium or sodium aluminates, which are able to conduct the current, but not to dissolve the sponge-zinc electrodes after discharging.

Manufacture of Spongy-Lead Plates for Storage Batteries. H. W. Butler and J. H. May, London, England. Patent No. 715,016, December 2, 1902. Application filed January 2, 1901.

The invention consists in the employment of powdered carbon (preferably charcoal) in the proportion of 10 per cent., mixed with 90 per cent. of lead oxide as paste or active material for storage-battery plates. The mixture in the above proportions is formed into a paste by the addition of dilute sulphuric acid, and pasted in the ordinary manner on the gird or conducting support of the plate. The plate is then placed in a forming solution, which may consist of dilute sulphuric acid only or dilute sulphuric acid containing a salt rich in oxygen, such as sodium nitrate. It is then connected with the positive pole of a source of electricity, a lead sheet being used as cathode, and the current having a density of about 1 ampère for 100 square inches of plate surface, until the carbon has become sufficiently oxidized, this being indicated by gas liberated from the surface of the plate. If sodium nitrate had been added to the electrolyte a new solution of dilute sulphuric acid must then be provided, and a current is passed in the opposite direction, until the active mass is reduced to spongy lead. The inventors are aware that it has been before proposed to use carbon in the form of small particles added to the paste, and their invention is said to consist "in the subsequent removal (either wholly or partially) of the carbon or equivalent by oxidation by electric action, and then the reduction of the porous mass thus formed to spongy lead by reversal of the electric current."

Accumulator Electrode. R. A. Katz, Berlin Germany. Patent No. 715,332, December 9, 1902. Application filed August 21, 1899.

This plate is shown in cross section in Fig. 6, and is built up of a non-conducting frame A in the form of a wide-meshed grating, which forms the support for the active material. It can be formed in one piece out of caoutchouc, celluloid or other acid-proof, non-conducting material. Against the frame A rest two thin perforated lead plates C, one on each face, which cover in the active material, and through their many

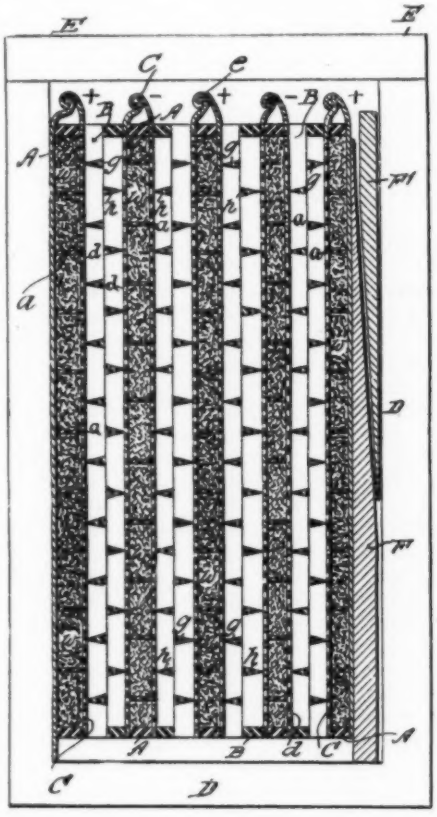


FIG. 6—STORAGE-BATTERY ELECTRODE.

narrow perforations allow access of acid to it. B represents separators, also of non-conducting, acid-proof stiff material, which serve at the same time to afford space for the acid, to keep the positive and the negative plates properly spaced from each other, to press the lead plate against the active material, to assist in supporting the lead plate and, indirectly, also to support the active material. They consist of two superposed gratings *g* and *h*, placed so that the intersections of the one cross the spaces of the other. As advantages are claimed the lightness of the accumulator and the possibility of easily exchanging the lead plates if necessary.

Accumulator. F. N. Blanc, Paris, France. Patent No. 715,343, December 9, 1902. Application filed February 17, 1902.

This invention covers a plate made up of a core and frame of aluminium, which are entirely covered with lead. The covering is deposited on the aluminium core by plunging the core, which has previously been provided with a covering of copper by electrolysis, into a bath of molten lead. The covering must be continuous without a break, so as to remove all danger of the attack of the aluminium by the electrolyte. A coating of paste is then applied to both sides of the plate.

Storage Battery. L. Paget, New York, N. Y. Patent No. 715,412, December 9, 1902. Application filed September 8, 1899.

The inventor claims that important advantages are secured in storage batteries by the use of a certain silicated material, known as "tufa," as an absorbent material for holding the sulphuric acid or other electrolyte of the battery. He prefers to use a "tufa" obtained from Italy, and has obtained excellent results with "tufa" of probably volcanic origin from the neighborhood of Civita Vecchia. As advantages, he claims the possibility of using an acid of higher specific gravity, a better support for active material of the plates than when "tufa" is not used, and the prevention of fumes in charging a battery, so that a very strong current may be used in charging. He claims that "tufa" remains unchanged, while kieselguhr and pumice stone are liable to break up and form a thin, mud-like material.

Storage Battery. L. Paget, New York, N. Y. Patent No. 715,413, December 9, 1902. Application filed August 28, 1901.

This invention "relates to multiple-cell storage batteries—that is, storage batteries formed of two or more cells—the especial object of the invention being to provide a storage battery of large capacity, but of small size and weight in relation to its electrical output. Fig. 7 represents a plan view of such a multiple-cell battery, showing some of the plates in section. A is the cell casing, and is divided into five cells by the insulating partitions B of hard rubber or similar material. The

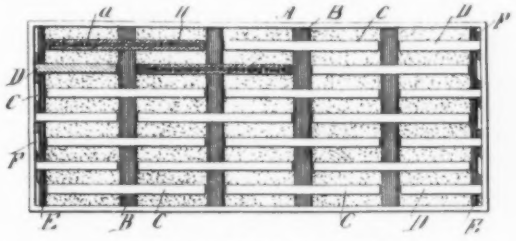


FIG. 7—MULTIPLE CELL BATTERY.

plates are arranged edgewise of the battery and the intermediate electrodes C extend through the partitions B, so that these intermediate electrodes are bipolar electrodes, with the ends of the plates forming the electrodes of opposite polarities. The end electrodes D also extend through insulating plates E at the end of the battery and connect with conducting plates F, provided with lugs for connections. The electrodes are shown as consisting of a supporting non-conducting frame 11, having a perforated web, filled with the active material *a*. Each of the compartments is filled with the electrolyte, which is preferably held or contained by an absorbent material G.

Storage Battery. E. J. Knapp, Chicago, Ill. Patent No. 716,056, December 16, 1902. Application filed May 19, 1902.

Buckling in storage batteries usually commences at the corners of the plates, and in order to prevent this triangular corner caps are employed made of substantially-rigid sheet rubber. There is claimed: "A storage-battery plate provided with constraining means at its corner portions for maintaining it in its normal plane against buckling or curling tendencies, the said means being in the form of corner caps."

GALVANIC CELLS.

Battery Depolarizer. C. E. Lockwood and W. C. Banks, New York, N. Y. Patent No. 714,590, November 25, 1902. Application filed September 5, 1900.

The oxide of copper depolarizer used in the ordinary batteries is prepared by oxidizing metallic copper, but as the process of oxidation never goes very deep into the copper, a good deal of it is inactive. The object of this invention has been to avoid the necessity of using this considerable body of useless metallic copper, and the inventors now propose to take

finely-divided particles of iron, then plate them with copper and convert the copper into oxide by heating the plated particles in a furnace.

Gravity Electric Battery. A. M. Friend, Denver, Colo. Patent No. 715,654, December 9, 1902. Application filed June 8, 1901.

The inventor proposes to overcome various troubles in gravity cells by dividing the cell horizontally into two compartments by a partition adapted to prevent the solid particles of matter from passing from one electrode to the other. The separating risk may consist of pasteboard or other suitable material possessing absorbent or porous property, and is of a size equal to the entire cross-sectional area of the cell.

Electric Battery. D. H. Wilson, Chicago, Ill. Patent No. 715,930, December 16, 1902. Application filed April 30, 1902.

The specification describes an improvement in the construction of the zinc carbon cells, by which a greater electrode surface is obtained. The zinc electrode is circular and the carbon electrode is constructed in such a shape that it surrounds, as it were, the zinc electrode on both sides.

MISCELLANEOUS.

Machine for Washing Matrices Preparatory to Electrotyping. C. M. Oliver, Baltimore, Md. Patent No. 713,671, November 18, 1902. Application filed August 26, 1902.

The object of the invention is to produce a machine which shall thoroughly and quickly wash away or remove all superfluous particles of black lead or any deleterious substance from the face of the matrix or mold, so that the electrodeposition of the metal on the matrix or mold may be unobstructed and a perfect electrotype copy of the original type-form may be had. For this purpose the inventor puts the molds to be washed face upward on a perforated table, which by means of a suitable mechanism is moved back and forth, while a number of perforated tubes are arranged above it, which spray the mold from all sides as it comes under them.

CURRENT NOTES.

At the December meeting of the Board of Directors of the American Electrochemical Society, the following applicants were elected to membership: Dr. Leonard Paget, New York; Prof. Dr. Julius Wagner, Leipzig, Germany; R. W. Vicarey, Stafford, England; Prof. Philippe A. Guye, Geneva, Switzerland; Leonard Wilson, Pittsfield, Mass.; Dr. William Dreyfus, New York; Charles J. Pretzfeld, Niagara Falls, N. Y.; August Eimer, New York; Dr. John Shields, London, England; Prof. D. McIntosh, Montreal, Canada; Dr. J. W. Walker, Montreal, Canada; Walter S. Landis, Bethlehem, Pa.; George P. Adamson, Easton, Pa.; Victor Engelhardt, Vienna, Austria; Dr. F. J. Machalske, Long Island City, N. Y.

The American Institute of Electrical Engineers has extended a cordial invitation to the members of the American Electrochemical Society, to attend the Institute meeting on Friday, April 17th; it will be remembered that the annual session of the Electrochemical Society will be held at New York City from April 16th to 18th. At the Institute meeting Mr. Wm. J. Hammer, of New York, will present a paper, illustrated by experiments and exhibits, on the subject of radio-activity and rays in general. Mr. Hammer recently visited Prof. Finsen's Institute at Copenhagen and made an investigation of his treatment of disease by ultra-violet rays; he also investigated the work being done by Prof. and Mrs. Curie at the Curie laboratory in Paris, and some important work that is being done in connection with the properties and applications of selenium. The full title of Mr. Hammer's paper is: "Notes on Radium and other Radio-active Substances, and a Consideration of Certain Phosphorescent and Fluorescent Substances;" "The Properties and Applications of Selenium;" "The Treatment of Disease by the Ultra-Violet Rays at the Finsen Institute, Copenhagen."

Making Steel in the Electric Furnace.—Just as we are going to press information reaches us that a test of new electric process of making steel has just been made in Lockport, N. Y. Among the gentlemen who are said to have witnessed the test, L. R. Wellman, of Cleveland, and John Fritz, of Bethlehem, are mentioned. The following claim is made: "The process saves 33 per cent. in fuel and nine-tenths in power."

Susquehanna River Power Plant.—A newspaper report states that "by the recent formal severance of the street railway system and the electric-light business of Baltimore, the initial step was taken in the $10,000,000 project of developing the water-power of the Susquehanna River and transmitting the same to Baltimore, Philadelphia and Wilmington." The power development of the Susquehanna River is watched with interest also in electrochemical and metallurgical circles.

CORRESPONDENCE.

FARADAY'S LAW AND THE THEORY OF ELECTRONS.

To the Editor of Electrochemical Industry.

Sir:—The article which appeared under the above title in the November issue of this magazine deserves commendation. Every effort to present in simple form the conclusions of scientific investigation is valuable to scientists in the factory, as well as to those in the university. In the writer's opinion, however, the law of Faraday may be explained in a manner still more simple than that of the article referred to. During recent years, as we are all aware, the general attitude toward the valence theory (better, "hypothesis") has undergone a change. Much as we realize its value to synthetical chemistry, we must admit that in the majority of cases constancy of valence is out of the question, and the reality of bonds is purely hypothetical. It is hoped that the following paragraphs will demonstrate the possibility of understanding Faraday's law without referring to the valence of individual elements and positive and negative bonds.

Faraday's Law.—A very satisfactory statement of this law is that made by Professor Nernst: "From the most diverse solutions the same amount of current liberates chemically equivalent amounts of the different ions." The amount of current is measurable, and experience tells us what the ions are; it only remains to determine what are chemically equivalent amounts of the different ions. The unit of comparison of the ions is the hydrogen ion. Any ion which carries the same charge as the hydrogen ion is equivalent to it; its valence is one. An ion carrying double the unit charge has a valence of two, etc. The determination of the number of unit charges carried by an ion (valence of the ion) is particularly simple, because of the close relation between acids, bases and salts, and is readily made clear.

In the solution of an electrolyte, the sums of all the positive and all the negative amounts of electricity must be equal, for the solution acts as electrically neutral. In a solution of hydrochloric acid (an *acid*), the total positive charge of the H ions must be numerically equal to the total negative charge of the Cl ions, and, since the same number of both ions are present, each Cl ion must carry an individual charge equal, but opposite in sign, to that of an H ion. In a sulphuric acid solution, however, the SO_4 ion must possess as much negative electricity as *two* H ions positive electricity, for the SO_4 ion is in combination with two H ions. In a CuCl solution *(salt)*, the Cu ion replaces the H ion of the acid (HCl), and must bear a charge equal to that of an H ion and equal, but opposite, to that of the Cl ion. In a $CuSO_4$ solution, the Cu ion has replaced two H ions; the Cu ion here must carry a charge double that of the H ion. A *base, e. g.*, NaOH, is referred to water, the hydroxide of hydrogen; the Na takes the place of

one H of the water, and the Na ion (as well as the OH ion) must carry a unit charge; it is univalent.

In the light of the above, *the number of unit charges carried by an ion is called the valence of that ion, and is equal to the number of hydrogen ions it is in combination with or takes the place of in the given electrolyte.* A gram ion (ionic weight in grams) of a bivalent ion is equivalent to two gram ions of a univalent ion. The same amount of electricity which discharges a gram ion of hydrogen will discharge only half a gram ion of a bivalent ion, or, in general, the ionic weight in grams, divided by the valence of the ion, is equivalent to one gram of hydrogen. Since one coulomb liberates .0104 mg. H, the number of milligrams of any ion liberated by one coulomb is .0104 multiplied by the ionic weight (H = 1) and divided by the ionic valence.

Theory of Electrons.—As for this recent theory of Nernst, its connection with the foregoing becomes at once clear when we are told that "electron" amounts to the same as "unit charge," viz.: that which makes an atom or group an ion. The valence of an ion may therefore be expressed in electrons, as well as in unit charges.

H. C. COOPER.

Syracuse University.

Book Reviews.

THE POTASH SALTS: THEIR PRODUCTION AND APPLICATION TO AGRICULTURE, INDUSTRY AND HORTICULTURE. By Dr. Lorentz Albert Groth, with a preface by Samuel Rideal, D.Sc. Lond., F.I.C. London: The Lombard Press, Ltd. 291 pages, illustrated.

This book is devoted to the description of potash salts, the methods by which they are obtained and prepared for the market and their application in the industries.

In the preface Dr. Rideal summarizes the general uses to which potash salts are placed in Great Britain. He calls attention to the pessimistic prophecy of Sir William Crookes in regard to the probable wheat famine of the world, and also calls attention to the renowned experiments carried on at Rothamsted. He finds that the consumption of potash in Ireland is very low, although this potash fertilizer is especially adapted to the potato, which is one of Ireland's chief agricultural products.

In regard to the salts of potash, this book treats of the supply in Canada, and shows that the quantity exported as hardwood ashes is continually decreasing, having amounted to 2,160 barrels in 1894 and only 1,323 barrels in 1898. In France about 2,000 tons of commercial potassium chloride is produced annually by the evaporation of sea water. India furnished about 20,000 tons of nitrate of potash, and about 1,200 tons of potash salts came from the mines at Kalusz in Galicia, the only potash mine in operation outside of Germany.

The historical sketch of the discovery of the natural potash salts is interesting, and shows that as early as 1452 the existence of these minerals was known, but their nature was unknown. The actual working of the mines for commercial purposes began in 1857. There are about 20 mines in all in operation. The dividends paid on the capital shares of the mines are apparently very satisfactory, ranging from 7 per cent., the lowest, to 17 per cent., the highest. The value of the output of the mines for 1902, based upon experience of previous years, is, in round numbers, $8,000,000.

Detailed descriptions of the operations of the mines, with sectional drawings and half-tone portraits of the machinery employed in the mines and in the purification of the salts, are interesting features of the book. A detailed description of all the different characteristics of salt mining is also given. A discussion of the geographical conditions which have made these deposits possible is also an interesting feature of the work. The potash salts are also discussed from a mineralogical point of view, the principal minerals found in the deposits being carnallite, sylvine, kainite, schoenite or pikromerite, polyhalite and kieserite. The different minerals are discussed in detail, both from a mineralogical and chemical point of view. A discussion is also given of the German Potash Syndicate, who practically control the output.

In metric tons, the total output of the mines for 1900 was as follows:

	Tons
Carnallite	1,697,803
Rock kieserite	2,047
Sylvinite	147,791
Kainite	1,189,394
Total	3,037,035

The amount of carnallite and rock kieserite used directly for agricultural purposes during the past year amounted to 55,489 tons in Germany, and in other countries 2,869 tons. For manufacturing concentrated salts, 1,641,493 tons were used. The amount of kainite and sylvinite used directly for agricultural purposes in Germany was 724,624 tons, and in all other countries 375,007 tons. For manufacturing concentrated salts, 237,554 tons were used, making a total of 1,337,185 tons.

In the potash mines are employed about 7,000 miners, and over 9,000 laborers are employed in the chemical works connected with them. The scientific corps numbers about 300 men. The works are supplied with 642 steam boilers, representing about 66,564 horse-power, and 924 steam engines, representing 59,420 horse-power. Attention is called to the fact that the formation of a syndicate has enormously increased the magnitude of the business and reduced the price of potash to Germans, while outside countries have been compelled to pay abnormally high prices in order to obtain their requirements. The great disadvantage arising out of such a procedure towards foreign agriculture and industry are apparent.

The part of the book devoted to the description of potash salts in industry is fully illustrated, and detailed descriptions are given of the chemical processes by which pure salts are obtained from the crude products. The electrochemical part of the industry is especially well developed. Attention is called to the fact that the history of electrochemistry began with Volta's great discovery, and attention is also called to the prophetic utterance of Davy, in 1806, when he said: "It is not improbable that the electrodecomposition of neutral salts, in different cases, may admit of economical uses." The output of the potash mines of Germany is closely associated with the electrolytic industry applying to salt, magnesium and the alkali and chlorine industry. The application of the electrolytic processes to these industries is briefly described.

From an agricultural point of view, the most important part of the work begins on page 117, with a description of the application of potash salts in agriculture. The consumption of pure potash (K_2O) for agricultural purposes is largest in Germany, amounting, in 1900, to 117,712 tons. The United States comes next in the magnitude of consumption, with 66,595 tons. France uses only 8,229, and Great Britain only a little over 7,200 tons. Portugal comes last on the list, with an annual consumption of 43 tons. In amount of potash (K_2O) consumed per 100 acres of land under cultivation, the consumption in Germany amounts to 298 pounds; in Holland to 312 pounds; in the United States of America to 42.2 pounds. Thus, while the United States comes next to Germany in the total amount consumed, by reason of the large area under cultivation, the amount per 100 acres consumed in this country is not a very high figure.

Detailed accounts of experiments with potash salts, taken from different authorities, are recorded.

The work is one of great value to the agricultural and technical student by reason of detailed study of the sources and methods of distribution of potash salts and the descriptions of technical processes, and especially on account of the statistics, which are difficult to obtain in the scattered form in which they have heretofore existed. The book will therefore be found useful to the chemist, the engineer and the farmer.

A NEW ACETYLENE TABLE LAMP.

The excellence of the acetylene light *per se* is so unquestionable that nobody can deny for a moment its enormous commercial possibilities, especially for certain purposes and for certain sections of the country where gas light and electric light are less convenient or entirely out of question. The all important commercial problem for the acetylene lamp manufacturer is at present to convince the general public that acetylene lighting is safe, and that the annoyances and accidents, formerly recorded in connection with the use of acetylene light, are not inherent in the use of acetylene, but were due to the use of inferior apparatus. The whole trouble was that the calcium carbide and acetylene industries developed too rapidly; attracted by the apparent simplicity of the problem, many incompetent inventors designed unsuitable and dangerous apparatus, with the result that the accidents which were due to poor designs and bad construction, were attributed by the public to the use of acetylene itself.

It is very gratifying to state that the conditions of the acetylene industry were very materially improved in recent years by the steady and painstaking work done by the competent engineers of this new industry. The problems involved in the use of acetylene light are now understood, and acetylene lamps are now made in accordance with scientific principles; as a result a steady and healthy growth of the industry is to be recorded. In the following we describe the most recent type of acetylene lamp made by Edward Miller & Co., of Meriden, Conn., for the Electrolite Gas Lamp Co. of New York City, by license under the Beck patents. One of the adjoining illustrations is a sectional cut, showing clearly all details of the design of the lamp; the other sketch shows the lamp separated for filling.

While at first sight of the sectional cut the lamp may look complicated, the operating parts are very few and simple. The lamp consists of three chambers, namely, a water chamber below, a carbide chamber above, and a movable gas holder which operates to bring the carbide into the water. The movable gas holder consists of a rubber bag and is fastened on the top wall of the carbide chamber. To this movable holder is fastened rigidly a feed stem which moves with the top wall of the gas holder and opens the feed when the gas holder is nearly empty and shuts off the feed when it is filled with gas.

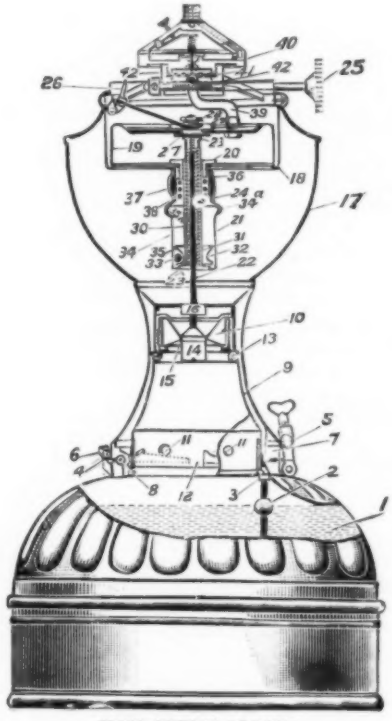
The gas in the lamp varies in pressure. Immediately before carbide is fed the pressure is less and as the carbide falls the pressure is raised slightly by the additional gas generated. The regulator or governor on the top of the lamp on to which the burner is fastened is an auxiliary means for keeping the flame uniform. It has absolutely nothing to do with the generation of gas. In the carbide chamber is located an auxiliary device named the "safety lock," which also has nothing to do with the operating of the lamp. Its function is to prevent further feeding when the lamp is tipped over so that the water cannot enter into the carbide chamber. It automatically arrests the further movement of the feed valve when the lamp is on its side, but permits the free movement thereof when the lamp is upright.

The gas after it is generated passes through the same opening through which the carbide falls and is dried by passing through the carbide and then screened by the felt filter. The mechanism in the top of the lamp over the gas bag is for the purpose of manually arresting the feed. When spindle 25 is turned inward the feed is positively shut off.

All the details of construction may be clearly seen from the sectional cut; 1 is the water fount. The round button 2 shows the height to which the water is filled; 3 is the joint ring on the fount; 4 is the loop into which hook 6 is passed in fastening the top to bottom of lamp; 5 is a clamp and screw which is thrown inward or outward in fastening or unfastening the top from the bottom part; 7 is the joint ring on the top part of the lamp which has cemented to it the round gasket 8; 9 is the stopper which carries the rubber feed valve 10. The stopper 9 has two lugs or projections 11, which are inserted into the slots 12, and is twisted to the left before taking it out or to the right after inserting it. The rubber valve 10 need not be removed at any time except when it is renewed.

The small gasket ring 13 on the stopper prevents the water running into the carbide when the lamp is tipped over; 14 is the metal feed valve which works up and down to close and open the carbide port 15; 16 is the auxiliary stop which registers in port 15 when the lamp is empty.

17 is the carbide holder; 18 is the top wall of the carbide holder which forms a receptacle for the flexible rubber gas holder or bag 19. The bag 19 is permanently secured to the lower side of 18 by means of the threaded nipple 20; 21 is the safety lock and filter combined and is located in the carbide chamber; 22 is the feed stem carrying metal valve 14 and auxiliary stop 16; 23 is the upper spring sleeve and is screwed on the top of feed stem 22; 23*a* is the lower spring sleeve.



CROSS SECTION OF LAMP.

24 is the feed spring which forces the gas out of the holder 19 into the burner. When carbide falls in the water, the gas inflates the holder 19 and expands spring 24, and as the gas passes out of the burner the spring contracts, deflates the holder 19, and forces feed stem 22 downward until an opening is made and carbide falls into the water. The gas so generated reinflates the holder 19 and the operation is repeated automatically until the carbide runs out or until the feed stem is forced upward by screwing in spindle 25.

26 is a bell crank lever pivoted at the side in the bag chamber and in engagement with the top of the bag. The feed stem 22 is screwed into nipple 27 and fastened with a lock nut 28. Nipple 27 is fastened in the top wall of bag by means of nut 29. Under this nut 29, lugs are placed with which the bell crank lever 26 engages.

30 indicates a sleeve which covers the feed spring 24 and is part of safety lock. The upper end of sleeve 30 is secured to the feed stem 22 between spring sleeve 23 and bag nipple 27, so that it has to move with the feed stem and the top wall of holder 19. On the lower end of this safety lock sleeve

is fastened a round metal part 31 with groove 32. In this groove rests a steel ball 33. Around this feed mechanism and safety lock is a casing 34, forming a cage for the ball 33. Immediately above the lower part of this casing 34 is an annular enlarged channel 34*a*. If for any reason the lamp is on its side and in operation, the feed mechanism will continue to move until the opening is made in the carbide port 15, but instead of the carbide falling by reason of the position of the lamp, water will run into port 15 and attack the carbide. Gas will instantly be generated and the holder 19 be inflated to its full capacity, and as the feed mechanism and that part of the safety lock carrying ball 33 are fastened to the top wall of bag 19, part 31, carrying ball 33, will be taken upward to a point parallel with part 34*a*, and the ball 33 will fall from the groove 32, into the annular channel 34*a*. As soon as the gas has burned out to permit the spring to contract the top of the bag, the feed stem and safety lock device will move downward again, but as the ball 33 has fallen into the channel 34*a*, and projects into the path of part 31, the upper part of 31 indicated by 35, will strike against the ball and wedge it between 35 and the edge of channel 34*a*, indicated by 35*a*, and prevent the further opening of the feed port 15. The gas remaining will pass out and burn and the flame go out.

36 is the upper part of casing 34 which carries the felt filter 37, through which the gas has to pass on its way to the holder 19. In this casing are holes 38, which admit the gas. This casing 34 serves: first, to hold the bag 19 in place; second, as a filter; third, as a safety lock, and fourth, as a guide and holder for the feed device; 39 is a flexible tube through which the gas passes from the bag or holder 19 on its way to the burner; 40 is the regulator or reducing valve which serves to give a uniform burning pressure. Below this regulator is another filter 41 in box 42. Box 42 also serves as a support for the shut-off spindle 25. By removing the top perforated cap of the lamp when burning, the operation of the bag 19, bell crank 26, and shut-off screw may be seen.

LAMP SEPARATED FOR FILLING.

The second sketch shows how the lamp is separated for filling. The shade is removed; the top is separated from the bottom part of the lamp and the top part is set upside down on the shade ring, as shown in the figure. The stopper is then removed from the top part, carbide is poured in and the stopper is replaced. The residue is then poured out from the lower fount, and the fount is washed both inside and outside; fresh water is then filled in. The residue is a good fertilizer or disinfectant for toilets.

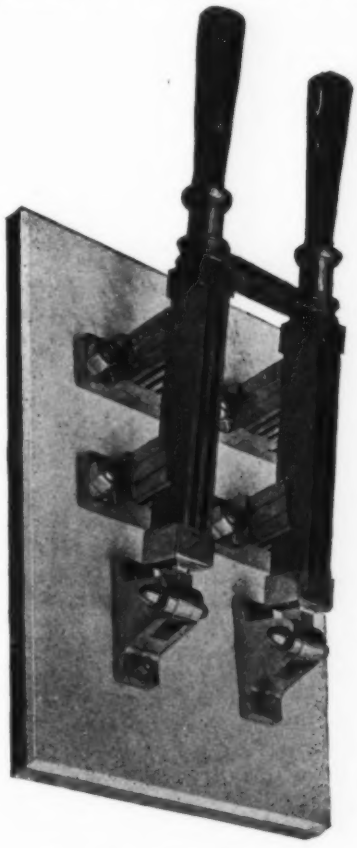
The lamp has been accepted by the consulting engineers of the National Board of Fire Underwriters, and is included in the list of permited acetylene devices issued by them.

1,500 AMPÉRE SWITCH.

Electrochemical work is essentially large current work and, therefore, apparatus and appliances for electrochemical plants must be designed just with this point in view.

The adjoining diagram shows the standard Eyanson switch for 1,500 ampères, as made by George T. Eyanson & Co. in Philadelphia, for use in electrochemical plants. All switches, made by this firm for 800 ampères and over, are made up of multiple blades, to insure ample contact surface and ventilation of the parts.

The blades and clips used give a large capacity switch in a comparatively small area. The switch is rated at 1,000 ampères per square inch of cross section, and 50 ampères per square inch of contact surface. The blades and dips are of cold rolled copper and all other current carrying parts of cast copper.



1,500 AMPERE SWITCH.

POROUS DIAPHRAGMS.

Porous diaphragms are of very great importance for many electrolytic processes in which the anodic and cathodic portions of the electrolyte are to be kept separate. The quality of the porous diaphragm very often determines the degree to which a certain electrolytic process is successful. In recent years the well-known firm of Villeroy & Boch, in Mettlach, Germany, have made extended researches with a view of finding the best conditions of making a porous diaphragm for use in acid solutions, which shall have at the same time a low electric resistance, a small mechanical permeability, and a long life. From the results of tests made by Dr. Max LeBlanc, and extending over a long time, it appears that the manufacturers have successfully solved this problem. Dr. LeBlanc used these diaphragms in a process of electrically reoxidizing the reduced chromic acid resulting from its use as an oxidizing agent in many industries. Some details given by him in the behavior of these diaphragms are of great interest.

Two different compositions were tried. The older composition was 75 per cent. of SiO_2 and 25 per cent. Al_2O_3. In the newer type about 2 per cent. of the Al_2O_3 is replaced by alkali. The newer plates are superior to the older ones, in so far as they have a smaller electrical resistance (this means, of course, that the resistance of the electrolyte in the dia-

phragm is smaller, as the diaphragm itself acts as an insulator). With a current density of 300 ampère per square centimeter a plate of 5 mm. (or 1-5 inch) thickness showed a drop of potential of 0.4 volt with the older chemical composition, and a drop of only 0.17 volt with the newer composition.

The plates have a different mechanical permeability according to the size of the pores. Diffusion is much smaller through plates with very fine pores than through plates with larger pores. An interesting conclusion reached by Dr. LeBlanc is that it is possible to make a diaphragm which has at the same time a very low electrical resistance and a very small mechanical permeability. In the latest type of diaphragm the pores are so small that they cannot be seen with the bare eye. The diaphragms are claimed to be thoroughly acid-proof and to last practically an infinite time in acid solutions; they are, however, not suited for alkaline solutions.

Messrs. Villeroy & Boch make such porous diaphragms up to the following maximum sizes: rectangular plates 23⅝ inches x 15 inches; square plates 23⅝ inches x 23⅝ inches; cylinders of 27½ inches height and 11⅞ inches diameter; boxes, 29½ inches by 29½ inches by 4 inches.

DIGEST OF U. S. PATENTS PRIOR TO JULY, 1902.

Compiled by Byrnes & Townsend, Patent Lawyers, National Union Building, Washington, D. C.

This digest of electrochemical United States patents prior to July, 1902, will be one by classes, setting out for comparison in each class those devices which have the same object, or those methods which seek the same results. In each class the patents will be arranged chronologically. The digest will be complete in the sense of covering every point which is touched upon in the original specification.

CAUSTIC ALKALI AND CHLORINE PROCESSES *(Continued).*

508,241. James C. Richardson, London, England, November 17, 1893.

Narrow, rectangular cathode bells, with flared lower ends. Bells open at the upper end, and provided with side outlets for caustic. Cathodes, horizontal grids of copper strips in the flared lower ends of the bells. Anodes, horizontal carbon rods, extending from lead plugs seated in the side wall of cell and serving as terminals.

508,804. Henry S. Blackmore, Mount Vernon, N. Y., November 14, 1893.

Apparatus consists of three rectangular vessels, arranged in a row and connected by siphons. Each siphon is a flat tube, of the width of the vessel, and has an exhaust pipe connected to its bend and a valve at one end. Intermediate vessel contains brine; end vessels, water only. Anode and cathode, perforated, inclined plates in the end vessels, respectively. Perforated salt reservoir depends into middle vessel, and has a steam coil within it. Device for maintaining a constant level in each vessel, and outlets for electrolytic products from end vessels.

510,834. Henry S. Blackmore, Mount Vernon, N. Y., December 12, 1893.

Cell divided by parallel vertical diaphragms into three compartments. Electrolyte fed into one end of middle compartment, any overflow escaping at the other end. End compartments contain water only, and have constant level devices and outlets for electrolytic products. Anode and cathode, serrated, vertical plates in end compartments, respectively. Hydrometer in cathode compartment to show level of caustic. Maintains water level in end compartments slightly above brine level to hinder passage of brine through diaphragms.

510,900. Elisha B. Cutten, New York, N. Y., December 19, 1893.

Iron vessel, serving as cathode, closed at top by an earthenware bell, with water-seamed inlet for brine and exhaust pipe for chlorine. Cathode, a series of vertical carbon bars, supported on an earthenware disc and having carbon pins extending through the disc into a mass of insulation. Insulated wires extend from terminal out through side of vessel. Cathode support rests on a disc of wire gauze, which permits caustic accumulating in bottom of cell, to be drawn off through a central discharge pipe.

511,682. Antoine J. O. Chalandre, Paris, France, December 26, 1893.

Anode compartment, a rectangular box built of non-conducting plates, with rubber packing. A number of inclined porous tubes, arranged in vertical rows, pass through opposite sides of the box. Vertical carbon anodes between the rows of tubes. Cathodes, a series of vertical sheet-iron combs, the teeth of which extend into the tubes. Hood for collecting hydrogen covering higher ends of tubes. Brine circulates between anode compartment and a separate saturating vessel.

512,266. Emile Andreoli, London, England, January 9, 1894.

Rectangular iron vessel, serving as a principal cathode. Supplemental cathode, also a rectangular box, of porous carbon, one or more layers of fine wire gauze, or two layers of wire gauze, with an intermediate space filled with crushed coke or iron filings, arranged within the outer vessel. Anodes of carbon or a basket of platinum gauze. Modification, with slate vessel containing vertical metal-plate cathodes and supplemental porous catnodes. The supplemental cathodes are connected to the principal cathodes by a fine wire, the resistance of which is calculated to shunt the desired current. Made electrolyze sulphates, nitrates, etc.

514,318. Greenwood Division of 489,677.

Cathode, a body of carbon having a cavity or space, the surface of which is electroplated with copper. A copper rod or plate conductor is soldered to the copper deposit.

514,681. Ernest A. Le Sueur, Ottawa, Canada, February 13, 1894.

Stoneware cover of the cell has a cam-ring support for anode. Rotation of the ring adjusts vertical height of anode. The upper surface of cam ribs is also inclined transversely, so that the anode can be tilted to immerse all parts equally in the brine.

518,040. Ernest A. Le Sueur, Ottawa, Canada, April 10, 1894.

Double diaphragm, consisting of spaced sheets of asbestos clamped against opposite faces of a lead frame by non-conducting side frames. Intermediate space filled with brine, maintained at a higher level than in anode and cathode compartments, or with a liquid of greater specific gravity than that in said compartments, thus preventing percolation of anode and cathode solutions into the diaphragm. The entire supply of brine may be fed into the diaphragm, and through it to the cell compartments.

518,785. Ernest A. Le Sueur, Ottawa, Canada, April 24, 1894.

Similar to 518,040. Anode side of diaphragm, a sheet of abestos or porous clay; cathode side, a sheet of parchment, bichromated gelatine or thick cloth, against which is clamped the cathode, of iron netting. May subdivide diaphragm space by a second sheet of asbestos.

520,257. Thomas Craney, Bay City, Mich., May 22, 1894.

Iron containing vessel, connected as cathode. Anode vessel, with curved bottom, of asbestos, cotton or sand, supported by a sheet of cotton cloth on a net and frame-work of iron, in electrical contact with the iron vessel. Anode, a layer of broken gas carbon resting on the asbestos, current being fed to it through a number of perforated clay tubes filled with carbon. Circulation of brine through anode chamber, and of water through cathode chamber. Several cells may be connected by pipes with rubber sections, enabling caustic to flow from cell to cell, or any cell to be cut out for repair. Exhausts chlorine by a fan.

[To be continued.]